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Attorneys for Plaintiff
HEWLETT-PACKARD COMPANY

UNITED STATES DISTRICT COURT

NORTHERN DISTRICT OF CALIFORNIA

CPVT

HEWLETT-PACKARD COMPANY, a Delaware corporation, Plaintiff, v. LEXJET CORPORATION, a Florida corporation, and LEXJET SOUTHERN CALIFORNIA, LLC, a California limited liability company, Defendants.	Case No. C08 02596 PVT **COMPLAINT FOR PATENT INFRINGEMENT** **DEMAND FOR JURY TRIAL**

Plaintiff HEWLETT-PACKARD COMPANY ("Hewlett-Packard") for its complaint against defendants LEXJET CORPORATION and LEXJET SOUTHERN CALIFORNIA, LLC (collectively "LexJet") alleges as follows:

PARTIES

1. Plaintiff Hewlett-Packard is a Delaware corporation with its principal place of business at 3000 Hanover Street, Palo Alto, California 94303.

2. Hewlett-Packard provides technology solutions to consumers, businesses and institutions globally, with offerings that span information technology infrastructure, global services, business and home computing, and imaging and printing. Hewlett-Packard owns valuable intellectual property rights in these technology areas.

3. On information and belief, defendant LexJet Corporation is a Florida corporation with its corporate headquarters at 1680 Fruitville Road, 3rd Floor, Sarasota, Florida 34236.

4. On information and belief, defendant LexJet Southern California, LLC is a California limited liability company, wholly owned by LexJet Corporation, with its principal place of business at 204 West Carleton Avenue, Orange, California 92867.

5. On information and belief, LexJet is a provider of imaging solutions, including ink-jet inks employed in thermal ink-jet printing with reduced color bleed and/or increased wettability and cloud point.

JURISDICTION AND VENUE

6. This action arises under the patent laws of the United States, 35 U.S.C. §§ 1 *et seq*., for infringement by LexJet of patents owned by Hewlett-Packard. This Court has jurisdiction over the subject matter of this action pursuant to 28 U.S.C. §§ 1331 and 1338.

7. This Court has personal jurisdiction over LexJet because LexJet does business in California and has sufficient contacts with the State of California to satisfy both the requirements of due process and Rule 4(k)(2) of the Federal Rules of Civil Procedure.

8. Venue is proper in this judicial district pursuant to 28 U.S.C. §§ 1391(b) & (c) and 1400(b).

INTRADISTRICT ASSIGNMENT

9. Pursuant to Civil L.R. 3-2(c), this action for patent infringement is subject to assignment on a district-wide basis.

COUNT ONE

(Infringement of U.S. Patent No. 5,116,409 by LexJet)

10. Hewlett-Packard realleges and incorporates by reference the allegations stated in paragraphs 1 through 9.

11. Hewlett-Packard is the owner of United States Patent No. 5,116,409 (the '409 patent), entitled "Bleed Alleviation in Ink-Jet Inks." The '409 patent was duly and legally issued by the Patent and Trademark Office on May 26, 1992. A true and correct copy of the '409 patent is attached as Exhibit 1.

12. LexJet has infringed and continues to infringe the '409 patent by making, using, offering for sale and/or selling products, including ink-jet inks, in the United States that embody or otherwise practice one or more of the claims of the '409 patent, or by otherwise contributing to infringement or inducing others to infringe the '409 patent.

13. On information and belief, LexJet's infringement has been with full knowledge of the '409 patent and willful.

14. LexJet's infringement has injured and damaged Hewlett-Packard. Hewlett-Packard is entitled to recover damages adequate to compensate Hewlett-Packard for LexJet's infringing activities in an amount to be determined at trial, but in no event less than a reasonable royalty, together with interest and costs.

15. LexJet's acts of infringement will continue unless and until enjoined by this Court, irreparably damaging Hewlett-Packard.

COUNT TWO

(Infringement of U.S. Patent No. 5,626,655 by LexJet)

16. Hewlett-Packard re-alleges and incorporates by reference the allegations stated in paragraphs 1 through 15.

17. Hewlett-Packard is the owner of United States Patent No. 5,626,655 (the '655 patent) entitled "Use of Co-Surfactants to Adjust Properties of Ink-Jet Inks." The '655 patent was duly and legally issued by the Patent and Trademark Office on May 6, 1997. A true and correct copy of the '655 patent is attached as Exhibit 2.

18. LexJet has infringed and continues to infringe the '655 patent by making, using, offering for sale and/or selling products, including ink-jet inks, in the United States that embody or otherwise practice one or more of the claims of the '655 patent, or by otherwise contributing to infringement or inducing others to infringe the '655 patent.

19. On information and belief, LexJet's infringement has been with full knowledge of the '655 patent and willful.

20. LexJet's infringement has injured and damaged Hewlett-Packard. Hewlett-Packard is entitled to recover damages adequate to compensate Hewlett-Packard for LexJet's infringing activities in an amount to be determined at trial, but in no event less than a reasonable royalty, together with interest and costs.

21. LexJet's acts of infringement will continue unless and until enjoined by this Court, irreparably damaging Hewlett-Packard.

PRAYER FOR RELIEF

WHEREFORE, Hewlett-Packard requests that the Court enter judgment in favor of Hewlett-Packard and against LexJet as follows:

(a) adjudicating and declaring that LexJet has infringed, contributorily infringed, and actively induced others to infringe the '409 and '655 patents;

(b) preliminarily and permanently enjoining LexJet and its officers, directors, agents, servants, employees, parents, subsidiaries, principals and all persons in active concert or participation with them from further infringement of the '409 and '655 patents;

(c) awarding Hewlett-Packard damages in an amount sufficient to compensate Hewlett-Packard for LexJet's infringement, contributory infringement, and active inducement of others' infringement of the '409 and '655 patents, but not less than a reasonable royalty;

(d) awarding pre-judgment interest, costs, and expenses to Hewlett-Packard pursuant to 35 U.S.C. § 284;

(e) awarding increased damages, pursuant to 35 U.S.C. § 284, by reason of LexJet's willful infringement of the '409 and '655 patents;

(f) declaring this case exceptional under 35 U.S.C. § 285 and awarding Hewlett-Packard its reasonable attorney fees, expenses, and costs incurred; and

(g) granting Hewlett-Packard such other and further relief as this Court may deem just and proper, or that Hewlett-Packard may be entitled to as a matter of law or equity.

Dated: May 22, 2008

Respectfully submitted,

MORGAN, LEWIS & BOCKIUS LLP

By ______________________

Michael J. Lyons
(State Bar No. 202284)

Attorneys for Plaintiff
HEWLETT-PACKARD COMPANY

DEMAND FOR JURY TRIAL

Hewlett-Packard hereby requests a trial by jury.

Dated: May 22, 2008

Respectfully submitted,

MORGAN, LEWIS & BOCKIUS LLP

By

Michael J. Lyons
(State Bar No. 202284)

Attorneys for Plaintiff
HEWLETT-PACKARD COMPANY

US005116409A

United States Patent [19]

Moffatt

[11] Patent Number: 5,116,409

[45] Date of Patent: May 26, 1992

[54] **BLEED ALLEVIATION IN INK-JET INKS**

[75] Inventor: **John R. Moffatt**, Corvallis, Oreg.

[73] Assignee: **Hewlett-Packard Company**, Palo Alto, Calif.

[21] Appl. No.: **686,731**

[22] Filed: **Apr. 17, 1991**

[51] **Int. Cl.**^{5} **C09D 11/02**

[52] **U.S. Cl.** **106/22**; 106/20

[58] **Field of Search** 106/20, 22, 23, 27

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,642,502	2/1972	Schneider	106/23
4,026,713	5/1977	Sambucetti et al.	106/23
4,400,216	7/1983	Arora	106/23
5,019,166	5/1991	Schwarz	106/22

Primary Examiner—William R. Dixon, Jr
Assistant Examiner—Helene Klemanski

[57] **ABSTRACT**

Color bleed (the invasion of one color into another on the surface of the print medium) using ink-jet inks is alleviated by employing zwitterionic surfactants (ph-sensitive or pH-insensitive) or ionic or non-ionic amphiphiles. The inks of the invention comprise a vehicle and a dye. The vehicle typically comprises a low viscosity, high boiling point solvent, one or two amphiphiles at concentrations above their critical micelle concentration (cmc), while the dye typically comprises any of the dyes commonly employed in ink-jet printing. The amount of surfactant/amphiphile is described in terms of its critical micelle concentration (cmc), which is a unique value for each amphilphile. Above the cmc, micelles form, which attract the dye molecule and thus control the color bleed. Below the cmc, there is no micelle formation, and thus no control of the color bleed.

18 Claims, 3 Drawing Sheets

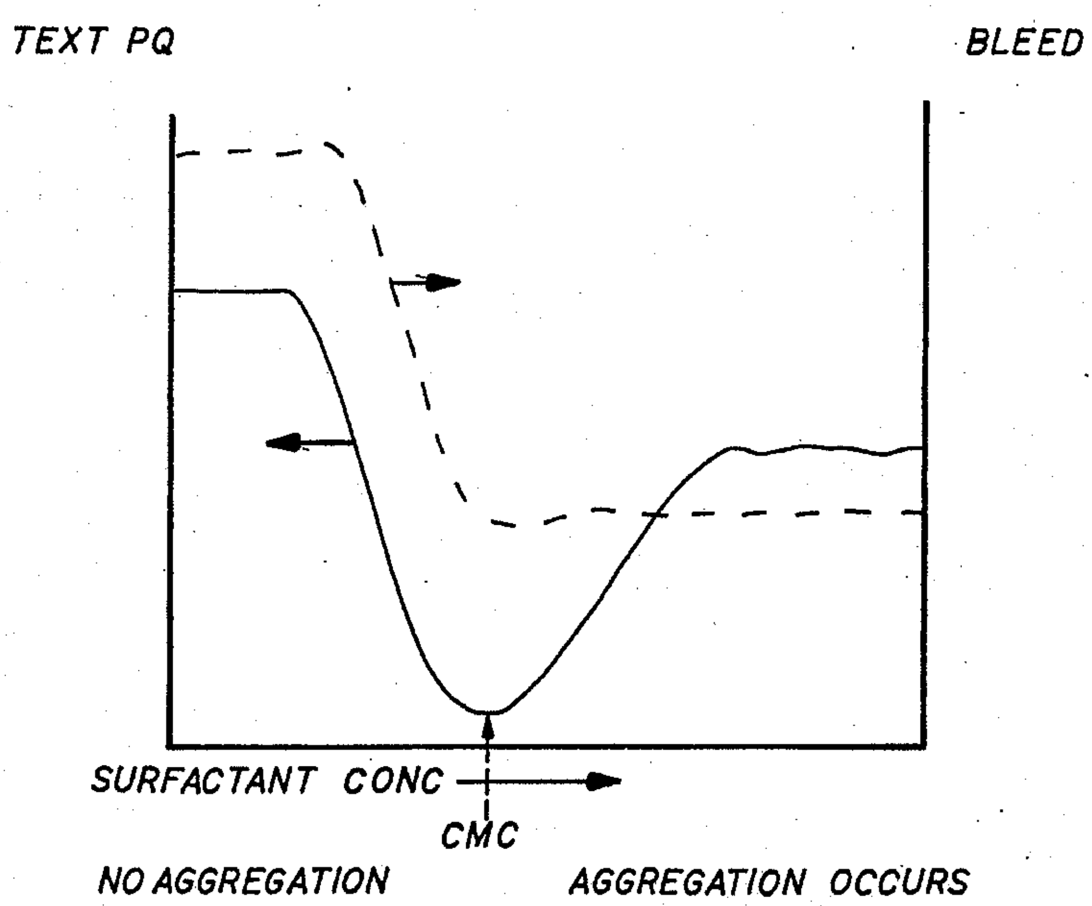
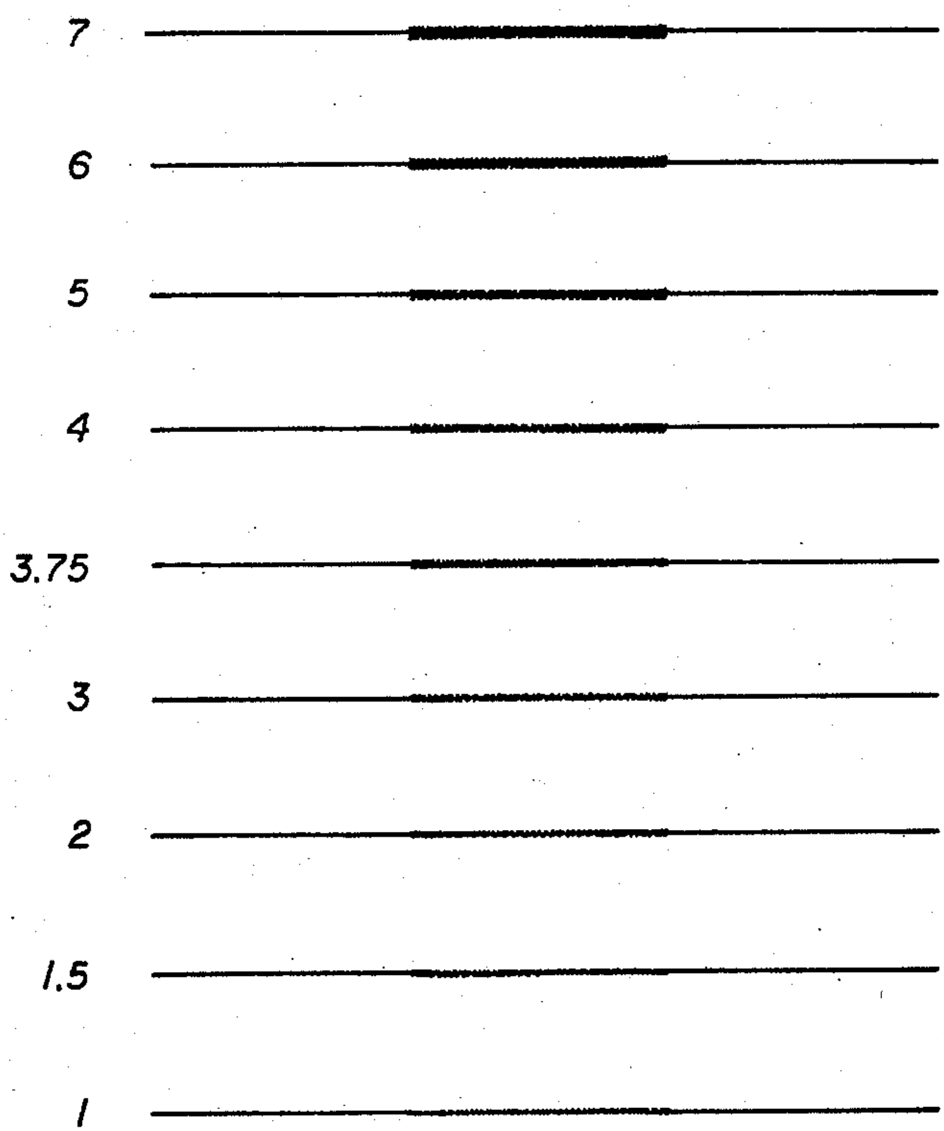


FIG. 1

BLEED INDICES REFERENCE



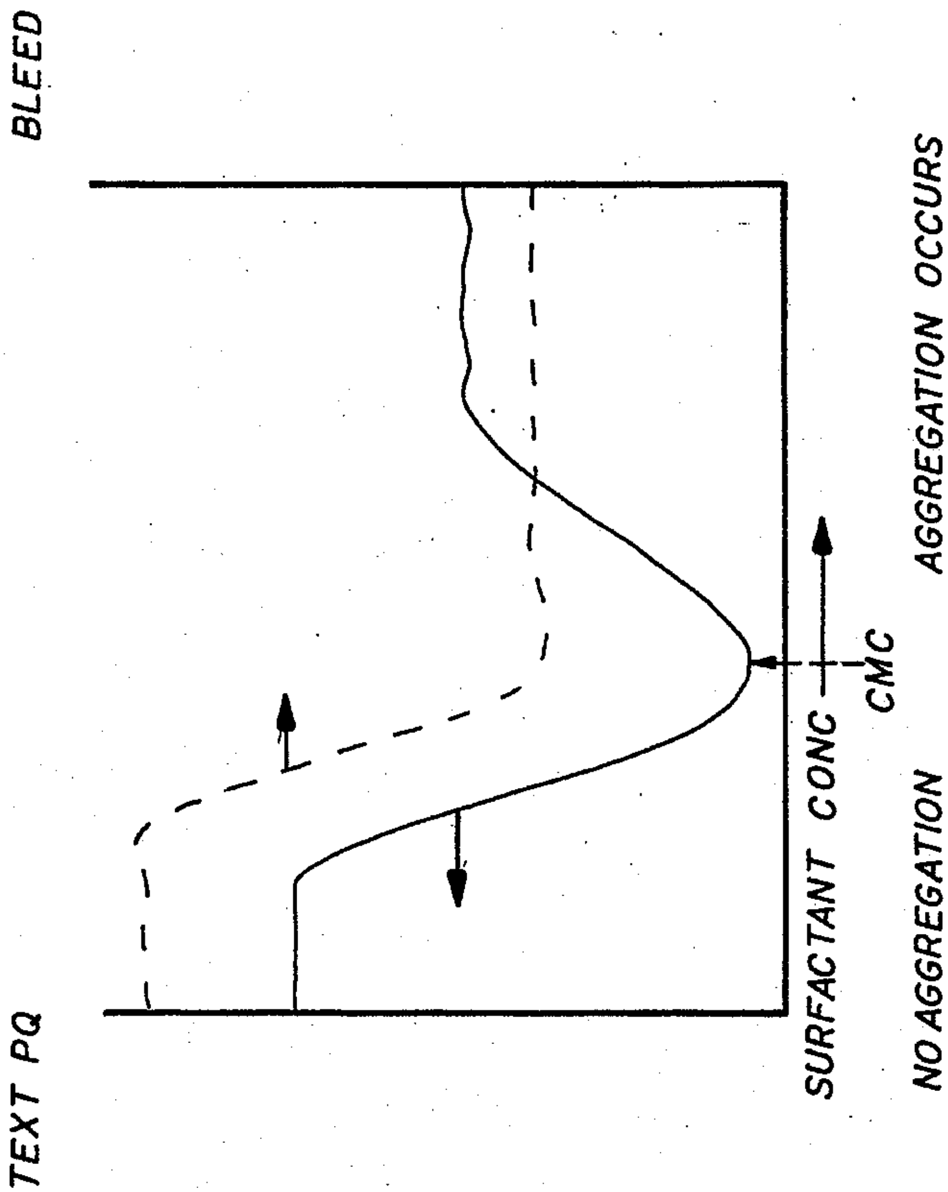

BLEED
TEXT PQ
SURFACTANT CONC
CMC
AGGREGATION OCCURS
NO AGGREGATION

FIG. 2

FIG. 3a

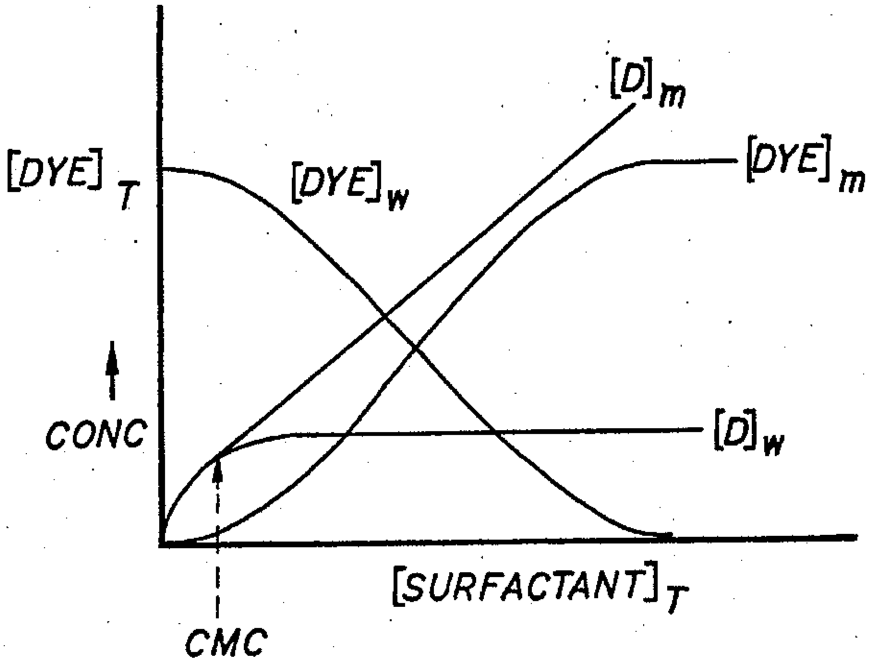
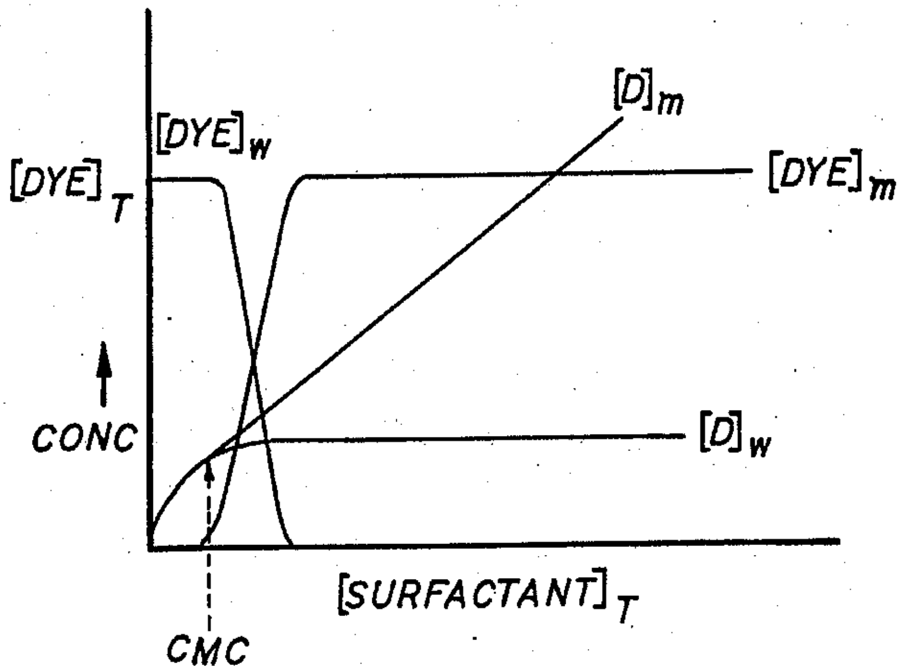

[D]m
[DYE]T
[DYE]W
[DYE]m
CONC
[D]W
[SURFACTANT]T
CMC

FIG. 3b


[D]m
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CONC
[D]W
[SURFACTANT]T
CMC

BLEED ALLEVIATION IN INK-JET INKS

TECHNICAL FIELD

The present invention relates to inks employed in ink-jet printing, especially in thermal ink-jet printing, and, more particularly, to colored ink compositions in which color bleed is substantially reduced or even eliminated.

BACKGROUND ART

Heavy dye loads on bond paper of various colored inks can lead to bleed and reduction of waterfastness. Bleed, as used herein, is the invasion of one color into another color on paper, which is a surface phenomenon. This is in contradistinction to uses of the term in the prior art, which tend to define "bleed" in the context of ink of a single color following the fibers of the paper; this is a sub-surface phenomenon.

Surfactants have been used as anti-clogging agents in Japanese Laid-Open Patent Application No. 63-165465 for use in ink-jet recording inks. The surfactants used in that application are limited to those having a surface tension between 20 and 50 dyne/cm. The amount of surfactant ranges from about 0.5 to 25 wt%. Specific examples disclosed include sodium dodecyl benzene sulfonate, sodium laurate, and polyethylene glycol monooleyl ether.

Japanese Laid-Open Patent Application No. 01-203,483 is directed to ink-jet recording compositions. Bleed reduction is mentioned in connection with printing using the inks. However, the compositions require pectin (0.01 to 2 wt%), which is probably being used as a thickener. However, pectin is not useful in inks used in thermal ink-jet printers, due to its thermal instability (it gels at higher temperatures).

Japanese Patent JO 1215-875-A is directed to inks suitable for ink-jet printing, evidencing good recording with fast drying without bleeding. The compositions all require triglycerides. Such compounds, however, are not stable to extended shelf life necessary for commercial inks.

Japanese Patent JO 1230-685-A is directed to inks suitable for ink-jet printing, evidencing quick absorption on the surface of conventional office paper without smear or blotting. The compositions comprise colorants and liquid solvents and/or dispersants and are characterized by the presence of a copolymer of ethylene oxide and propylene oxide of the formula $HO(C_2H_4O)_a-C_3H_6O(C_2H_4O)_bH$, where a+b is up to 50 and b is optionally 0. These copolymers are referred to as "PLURONICS". For the most part, they have not been found to stop bleed.

Thermal ink-jet printers offer a low cost, high quality, and comparatively noise-free option to other types of printers commonly used with computers. Such printers employ a resistor element in a chamber provided with an egress for ink to enter from a plenum. The plenum is connected to a reservoir for storing the ink. A plurality of such resistor elements are arranged in a particular pattern, called a primitive, in a printhead. Each resistor element is associated with a nozzle in a nozzle plate, through which ink is expelled toward a print medium. The entire assembly of printhead and reservoir comprise an ink-jet pen.

In operation, each resistor element is connected via a conductive trace to microprocessor, where current-carrying signals cause one or more selected elements to

heat up. The heating creates a bubble of ink in the chamber, which is expelled through the nozzle toward the print medium. In this way, firing of a plurality of such resistor elements in a particular order in a given primitive forms alphanumeric characters, performs area-fill, and provides other print capabilities on the medium.

Many inks that are described for use in ink-jet printing are usually associated with non-thermal ink-jet printing. An example of such non-thermal ink-jet printing is piezoelectric ink-jet printing, which employs a piezoelectric element to expel droplets of ink to the medium. Inks suitably employed in such non-thermal applications often cannot be used in thermal ink-jet printing, due to the effect of heating on the ink composition.

A need remains for ink compositions for use in ink-jet printing, particularly thermal ink-jet printing, which do not evidence bleed, as defined herein, and yet which possess relatively long shelf life and other desirable properties of such inks.

DISCLOSURE OF INVENTION

In accordance with the invention, color bleed on paper media printed by ink-jet is alleviated by employing nonionic, pH-sensitive or insensitive zwitterionic (amphoteric) surfactants, or ionic surfactants (amphiphiles or detergents). The ink comprises (a) 0 to about 20 wt% of one or more low vapor pressure solvents (b) one or more water-soluble dyes, (c) one or more self-aggregating or performed micellar, vesicular-like components (particular examples and concentrations to be specified below), and (d) a filler such as water and a biocide, fungicide, and/or slimicide. As used herein, the term "low vapor pressure solvent" refers to a solvent having a vapor pressure that is lower than that of water and the term "water-soluble dye" refers to a dye whose solubility in water exceeds 2 wt%.

Low vapor pressure solvents can include, but are not restricted to, glycols such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, polyethylene glycol, polypropylene glycol, and derivatives thereof; diols such as butanediol, pentanediol, hexanediol, and homologous diols; glycol esters such as propylene glycol laurate; mono and di glycol ethers such as cellosolves, including ethylene glycol monobutyl ether, diethylene glycol ethers such as the carbitols, diethylene glycol mono ethyl, butyl, hexyl ethers, propylene glycol ether, dipropylene glycol ether, and triethylene glycol ether; long chain alcohols such as butyl alcohol, pentyl alcohol, and homologous alcohols; and other solvents such as sulfolane, esters, ketones, lactones such as γ-butyro-lactone, lactams such as N-pyrrolidone and N-(2-hydroxyethyl)pyrrolidone, and glycerols and their derivatives.

Microbial reagents include, but are not limited to, NUOSEPT (Nudex, Inc., a division of Huls Americal, UCARCIDE (Union Carbide), VANCIDE (RT Vanderbilt Co.), and PROXEL (ICI Americas).

Dyes include, but are not limited to, anionic water-soluble types such as C.I. Acid Blue 9 (#42090), C.I. Acid Red 18 (#18), C.I. Acid Red 27 (#16185), C.I. Acid Red 52 (#45100), C.I. Acid Yellow 23 (#19140), C.I. Direct Blue 199 (#74190), C.I. Direct Yellow (#29325) and their monovalent alkali earth ions such as Na^{30}, Li^{30}, Cs^{30}, NH_4^+, and substituted ammonium salts. The dye(s) is present from about 0.1 to 10 wt% of the ink.

It is important to note that some ingredients have dual functions. For example, n-butyl carbitol can function as a low vapor pressure solvent and as a self-aggregating component. Further discussion concerning the critical role of aggregation and concentration of surfactants in alleviating bleed is provided below. It is sufficient to state here that critical concentrations of surfactant are necessary to efficiently and completely prevent bleed in double dot mode printing used to generate the print samples herein.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows bleed reference patterns where higher bleed indices reflect unacceptable bleed (a bleed score of <2.5 is considered to be acceptable for high quality text output);

FIG. 2, on coordinates of text print quality (left abscissa) or bleed (right abscissa) and surfactant concentration, shows the qualitative effect on print quality and bleed as a function of concentration of a surfactant; and

FIGS. 3*a*–*b*, on coordinates of dye concentration and total detergent (surfactant) concentration ($[D]_T$), are plots of dye adsorption to micelles, with FIG. 3*a* showing the effect of weak adsorption of dye to micelle and with FIG. 3*b* showing the effect of strong adsorption of dye to micelle, where $[D]_M$ is the detergent (surfactant) concentration in micelles and $[D]_W$ is the detergent (surfactant) concentration in water.

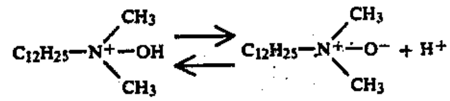
BEST MODES FOR CARRYING OUT THE INVENTION

In the practice of the invention, color bleed resulting from the use of ink-jet inks in thermal ink-jet printers is alleviated by employing either zwitterionic surfactants or non-ionic amphiphiles. The zwitterionic surfactants employed in the practice of the invention may be pH-sensitive or pH-insensitive.

All concentrations herein are in weight percent, unless otherwise indicated. The purity of all components is that employed in normal commercial practice for thermal ink-jet inks.

For convenience, examples of bleed alleviating surfactants are divided into two categories: (1) non-ionic and amphoteric and (2) ionic. The former class is further subdivided into three classes: (a) water-soluble amphiphile mimetics, such as STARBURST dendrimers, which are branched polyethylene amines available from Polysciences, Inc., and the like, (b) polyethers, such as ethylene glycol n-butyl ether, diethylene glycol n-butyl ether, diethylene glycol n-hexyl ether, triethylene glycol n-butyl ether, propylene glycol isobutyl ether, the TRITONS, which are nonyl phenyl polyethylene oxide surfactants available from Rohm & Haas Co., the PLURONICS and PLURAFACS, which are polyethylene oxide and polypropylene oxide block copolymers available from BASF, and the SURFYNOLS, which are acetylenic polyethylene oxide surfactants available from Air Products & Chemicals, Inc., and (c) amphoteric molecules, such as NDAO, NTAO, NHAO, OOAO, NOAO, and SB3-16; further information relating to these compounds is presented below. The ionic class, which comprises both cationic and anionic surfactants, also is represented by bile salts (sodium, lithium, ammonium, or substituted-ammonium cholate) and water-soluble dyes.

An example of a pH-sensitive zwitterionic surfactant is N,N-dimethyl-N-dodecyl amine oxide (NDAO), which has a pk_a in water of about 2.3:



This compound has a molecular weight of 229, and a critical micelle concentration (cmc; to be discussed in greater detail below) of 13 mM.

Also, in place of the $C_{12}H_{25}$- moiety, any R moiety may be used. The following moieties, their name, abbreviation, molecular weight (mw), and cmc are useful in the practice of the invention:

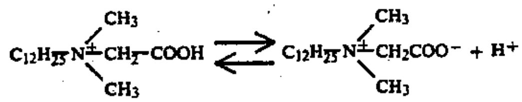
N,N-dimethyl-N-tetradecyl amine oxide (NTAO); mw =257; cmc =6-8 mM;

N,N-dimethyl-N-hexadecyl amine oxide (NHAO); mw =285; cmc =0.8 mM;

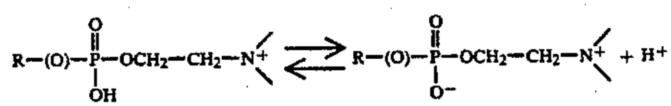
N,N-dimethyl-N-octadecyl amine oxide (NOAO); mw =313; cmc =small;

N,N-dimethyl-N-(Z-9-octadecenyl)-N-amine oxide (OOAO); mw =311; cmc =small.

Another example is N-dodecyl-N,N-dimethyl glycine, which has a pk_a of about 5 in water:

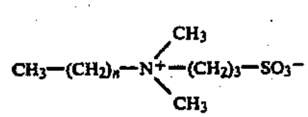


Yet other examples include phosphates, phosphites, phosphonates, lecithins or the like, and phosphate esters such as phosgomyelin which has a pk_a of about 2 to 3 in



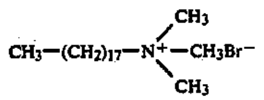
Other similar compounds include phosphoglycerides, such as phosphatidylethanolamines, phosphatidylcholines, phosphatidyl serines, phosphatidylinositols, and B'-O-lysylphosphatidylglycerols.

Additional examples of compounds that are useful in the practice of the invention include the sulfobetaines, which are zwitterionic, but pH-insensitive:



Where n=11, the compound is denoted SB3-12; where n=15, the compound is denoted SB3-16.

Examples of ionic surfactants that are suitably employed in the practice of the invention include such cationic compounds as



cetyl trimethylammonium bromide (CTABr), and such anionic surfactants as

CH_3-$(CH_2)_{11}$-O-$SO_3$$-$Na+*sodium dodecyl sulfate (SDS)*

CH_3-$(CH_2)_n$-$SO_3$$-$NA+sodium sulfonates

Examples of non-ionic, non-amphoteric surfactants useful in the practice of the invention include compounds available under the tradenames TERGITOL, which are alkyl polyethylene oxides available from Union Carbide, and BRIJ, which are also alkyl polyethylene oxides available from ICI Americas, having the formula:

$$CH_3—(CH_2)—(—O—CH_2—CH_2—)_m—OH$$

(where n=3 and m=2, this is n-butyl carbitol, a cellusolve).

Also included in this category are the PLURONICS and the PLURAFACS (BASF) having the general formula:

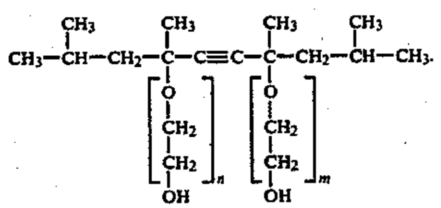
$$HO—(—CH_2—CH_2—O—)_n—(—CH_2—CH(CH_3.\ )_m—CH_2—CH_2—OH$$

The TRITONS (Rohm & Haas Co.) are generally represented as:

$$R—Ph—O(CH_2—CH_2—O)_yR'$$

where R, R' is any alkane, alkene, aryl or alkynyl group or H, Ph is phenyl, y=1 to 50, and R is para to the ether linkage on the benzene ring.

The SURFYNOLS (Air Products & Chemicals, Inc.) are represented as



where n+m=0 to 50.

EXAMPLES OF BLEED ALLEVIATING AMPHIPHILES

Zwitterionic surfactants, such as NDAO, NTAO, OOAO, and NOAO, were tried first. These surfactants (except for NOAO) are totally miscible in aqueous solutions (about 0.1 to 20 wt%) of diethylene glycol, glycerol, and ethylene and propylene glycol. NOAO is also miscible if up to about 10 wt% of a straight chain primary alcohol, such as n-propanol, n-butanol, n-pentanol, is added.

Four examples are included in Table I. NDAO concentrations at 0, 0.5%, 1.0%, and 5% surfactant in water was the vehicle. The colors were simultaneously printed side by side using a dot-on-dot (double pass) algorithm. The dyes used were 1.33% C.I. Acid Red 27 (#16185); 1.65% C.I. Acid Blue 9 (#42090); 1.33% C.I. Direct Yellow 86 (#29325). Table I shows that without NDAO, massive proliferation of the colors occurs (bleed). NDAO at 0.5% radically alters the extent of bleed, but it is not eliminated. Table I also shows the effect of increased NDAO concentrations of 1% and 5%, respectively, concentrations which substantially eliminate bleed. Vehicles which contained 0 to 20% of di-ethylene glycol, propylene glycol, or glycerol or 0 to 15% 1,5-pentanediol gave similar results with NDAO at approximately the same concentrations (see Table III below, Ink #1). NOAO and OOAO required 0 to about 10% of a co-solvent, such as 1-propanol, 1-butanol, or 1-pentanol, for solubility purposes (see Table III below, Inks #6–11, 13–16, 25–27, 29, 30, 31, 33).

The color bleed index values listed in Table I are derived from the scale provided in FIG. 1, which is a print of lines of red (magenta) ink on a background of yellow ink. For high text quality output, a value of ≦2.5 is considered to be acceptable. For somewhat lower quality demands, such as printing on boxes, plotting, and the like, a value of about 3 to 4 may be considered to be acceptable. Inks commonly used commercially presently have values, typically, of about 6 or more.

TABLE 1

Bleed Indices for Various Systems.

System[1]	Wt %[2]	Index[3]
NDAO	0	6.0+
	0.5	4.0
	1.0	2.5
	5.0	1.0
n-pentanol; 1-5-pentanediol	2.0; 6.0	6.0
n-pentanol; 1,5-pentanediol; NDEC[4]	2.0; 6.0; 2.0	2.0
CTABr	2.0	3.5
DEG; CTABr	6.0; 2.0	2.5
SDS	2.0	3.5
n-butanol; 1,4-butanediol; SB3-16	2.0; 5.0; 8.0	4.0
DEG; PLURONIC L-63	5.0; 5.0	2.5
1,5-pentanediol; SURFYNOL S465	10.0; 2.0	5.0
1,5-pentanediol; SURFYNOL S465	10.0; 4.0	2.0
TRITON CF-21	0.7	6.0+
	1.0	3.0
	3.0	2.0
DEG	5.5	6.0
n-butanol	7.0	5.0

Notes:
[1]Dyes include AR27, 1.33%; DY86-Na, 1.33%; AB9-Na, 1.65%.
[2]wt %, balance is water.
[3]Color Bleed Index; a value of ≦2.5 is considered acceptable for high quality text output.
[4]N,N-dimethyl-N-dodecyl-N-(ethyl carboxylate).

Also shown in Table I is an example in which the vehicle consisted of 2% n-pentanol and 6% 1,5-pentanediol or of 7% n-butanol. The use of such paper wetting and penetrating solvents in the inks alone does not alleviate bleed.

Table I shows the effect of employing a (betaine) zwitterionic surfactant (NDEC) in conjunction with a vehicle of 2% n-pentanol and 6% 1,5-pentanediol in stopping bleed. The addition of NDEC surfactant markedly reduces the extent of bleed, as compared to the vehicle without surfactant.

Not all zwitterionic surfactants are efficient at eliminating bleed. For example, a system comprising 2% n-butanol, 5% 1,4-butanediol, and 8% SB3-16 is not efficient as the other examples in alleviating bleed. On the other hand, while bleed is still present, it is reduced compared to that in which the vehicle is 5.5% DEG, where no surfactant was present.

Small amounts of cationic surfactants in ink also eliminate bleed. A degree of bleed control (3.5) is achieved using 2% cetyl trimethylammonium bromide (CTABr) in water. The addition of co-solvent to the vehicle,

specifically 6% diethylene glycol with CTABr present at 2%, provides even better bleed control (2.5) than afforded with CTABr alone.

Anionic surfactants in inks can control bleed as well. For example, 2% sodium dodecylsulfate (SDS) in water as vehicle controls bleed. Although the color bleed index is 3.5, such an ink would be acceptable for, e.g., plotters.

Only one non-ionic surfactant of the PLURONIC class, L-63, has been found to prevent bleed when present in the ink (see Table I).

Table I shows the effect of increasing SURFYNOL 465 concentration on eliminating bleed: 2% SURFYNOL 465 is not effective, but, 4% SURFYNOL 465 controls bleed well in ink vehicles containing 10% 1,5-pentanediol solvent.

Increasing concentrations of TRITON CF-21 detergent shows similar effects (cf. Table I).

These results show that different classes of surfactants exhibit concentration dependence on efficient bleed alleviation. Concentration effects were observed in the case of non-ionic surfactants, such as n-butyl carbitol, n-butyl propasol, and n-hexyl carbitol (not shown).

It is interesting to note common structural features among these bleed alleviating surfactants. All have features common among surfactants: long hydrocarbon (hydrophobic) tails with polar (hydrophilic) headgroups. Other such detergents of similar structures can be formulated in inks to solve bleed, provided they have structural features common to these. This does not imply that the bleed alleviating behavior is indigenous to all detergents.

The detection of the cmc or the onset of micellization in an ink can be determined by a number of methods. Typically, sharp changes are seen in plots of surface tension vs. surfactant concentration (in the ink) or osmotic pressure vs. surfactant concentration (in the ink). These sharp changes are attributed to the cmc. Other methods, such as conductivity, turbidity, determination of equivalent conductance are precluded in water-soluble inks.

Bleed Alleviation —Possible Mechanisms

Reference to FIG. 2 gives a hypothetical concentration of surface-active reagent versus bleed and text print quality scale profiles. Basically, this Figure profiles the bleed and text quality responses observed for all surfactants under investigation. FIG. 2 assumes that other coponents of the ink vehicle and dye(s) concentrations are fixed and that the surfactant concentration is the dependent variable. From FIG. 2, upon addition of a small amount of surfactant, there is little change in the bleed control and sharpness of the text print quality. With further additions of surfactant, degradation of text print quality results with little or no improvement (perhaps even a slight degradation in bleed alleviation occurs in some cases) in bleed. A surfactant concentration is finally achieved where the quality of text begins to improve and bleed is reduced. Further decreases in bleed and improvement of text quality may occur with increasing surfactant concentration in the ink.

The lowest surfactant concentration where bleed alleviation and improvement of text print quality becomes appreciably effective is found to be near the critical micelle concentration (cmc) or critical monomer concentration of most surfactants. (The cmc is the concentration of surfactant where simple electrolyte or non-electrolyte chemistry lessens in importance to colloid chemistry. For the simple surfactants previously described, this is the concentration of surfactant where micelles, or aggregated surfactant molecules, begin to appear.)

Micellization is driven by entropic constraints - the hydrocarbon chains are driven into the interior of the micelle with the hydrophilic, water-soluble groups driven to the exterior. The resulting domainal fluid provides regions of olefin-rich and water-rich pockets, which can compartmentalize organic solutes such as dyes, co-surfactants, and co-solvent molecules, depending on their hydrophobicity. In addition, micelles interact and find regions in solution where their positional (potential) energy is minimized. It is conceivable that micelles containing charged dye molecules behave in a similar fashion.

Inspection of Table II shows that the cmcs listed here nicely coincide with the onset of bleed alleviation in Table I. The cmcs indicated are for pure water. The tabulated cmc will differ from those in the ink because added salts and hydrophobes perturb micelle structure.

TABLE II

CMC Data for Surfactant Print Samples

Class / Surfactant	Mole wt.	[cmc][1], M	cmc[1], wt %
Zwitterionic:			
NDAO	229	0.013	0.3
$C_{13}H_{27}N(CH_3)_2(CH_2)_2COO^-$	285	0.015	0.5
SB3-12	335	0.012	0.4
Ionic:			
CTABr	364	0.0008	0.03
SDS	288	0.008	0.23
Non-ionic:			
SURFYNOL 465	634	0.03-0.05	2-3
TRITON CF-21	489	0.001	0.05
N-42	389	ca 0.001	0.04
Butyl carbitol	192	0.2-0.3	4-6

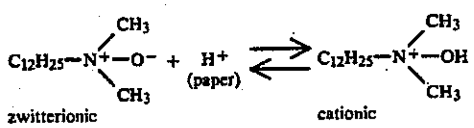
Note: [1]cmc in pure water at 25° C.

Incorporation of dyes into micelles is the probable method by which surfactant-containing inks control bleed. Micelles with dye of one color shot out of an ink-jet pen will not exchange dye of another color in an adjacent micelle on paper medium, because the rate at which the mobile medium evaporates or adsorbs into the paper is much faster than the desorption rate of the dye molecules from the micelles or the rate at which dye molecules diffuse through the micellar medium. Bleed alleviation results.

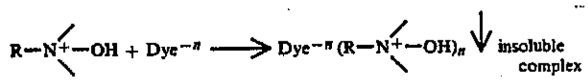
The efficiency of this bleed alleviation depends upon the level of adsorption of the dyes into the micelles, the number concentration of micelles in the ink, and the difusion of dye and micelles on the paper surface. FIGS. 3*a* and 3*b* show hypothetically the extent of adsorption of dye into micelles as a function of surfactant concentration for dye molecules that strongly adsorb to micelles (FIG. 3*b*) and for dye molecules that weakly adsorb (FIG. 3*a*). It will be noted that in the weakly adsorbing dye, a much higher surfactant concentration is necessary to bind the same amount of dye than in the case of the strongly adsorbing dye. Obviously, the propensity for dye to adsorb to micelles is a function of the structure (hydrophobicity) and interactions of the dye molecule, the surfactant, co-solvent, and co-surfactant (if any) present.

Thus, surfactant concentration affects bleed control. Higher concentrations of micelles absorb more dye molecules and slow their diffusion rate.

Additionally, certain pH-sensitive zwitterionic surfactants will pick up H+ from the paper and change it from a zwitterionic surfactant to a cationic one.



This occurs on the paper surface. Anionic dyes such as those mentioned above complex with this cationic surfactant on the paper surface to produce a water-insoluble complex of dye and surfactant, such as



Because these insoluble complexes do not diffuse, bleed control is achieved.

INDUSTRIAL APPLICABILITY

The ink compositions of the invention are expected to find use in thermal ink-jet inks, especially color inks, where bleed of one color into another is a concern. The ink compositions of the invention reduce or even eliminate such color bleed.

EXAMPLES

The following inks were prepared, as listed in Table III, below (the dyes and dye concentrations were as listed above and the balance was water):

TABLE III

	Ink Compositions.				
Ink #	Amp1	Amp2	NaCh[1]	Solvent1	Solvent2
1	NDAO 1%			DEG 6%	
2	S465[2] 1.5%			DEG 6%	
3	S465 1.5%			DEG 10%	
4	NTAO 1.0%	S465 0.5%		DEG 10%	
5	NDAO 2.5%	S465 1.0%		DEG 10%	
6	NOAO 4%			DEG 3%	n-BuOH[3] 7%
7	OOAO 2%			DEG 6%	n-BuOH 2%
8	NOAO 4%	S465 0.5%		DEG 6%	n-BuOH 7%
9	OOAO 2%	S465 0.5%		DEG 6%	n-BuOH 2%
10	NOAO 4%			DEG 6%	n-BuOH 7%
11	OOAO 2%	S465 0.5%	3.7%	DEG 6%	n-BuOH 2%
12	nBC[4] 6%				
13	NOAO 4%	S465 1%	0.5%	DEG 6%	n-BuOH 3%
14	NOAO 6%	nBC 6%	2%		n-BuOH 3%
15	OOAO 3%	S465 0.5%	0.5%	DEG 6%	n-BuOH 3%
16	OOAO 3%	S465 0.5%	0.5%	DPM[5] 6%	n-BuOH 3%
17	NOAO 6%	S465 0.5%	2%	1,4-BD[6] 5%	

TABLE III-continued

	Ink Compositions.				
Ink #	Amp1	Amp2	NaCh[1]	Solvent1	Solvent2
18	NOAO 6%	S465 1%	2%	1,4-BD 5%	
19	OOAO 6%	S465 0.5%	0.5%	DEG 5.7%	
20	OOAO 3%	S465 0.5%	0.5%	DEG 5.7%	
21	OOAO 3%	S465 05%	LiCh[7] 0.5%	DEG 6%	
22	L63[8] 6%				
23	n-BuP[9] 5%				
24	nBC 8%				
25	OOAO 7%			1,4-BD 5%	n-BuOH 2%
26	NTAO 7%			1,4-BD 5%	n-BuOH 2%
27*	OOAO 3%	S465 0.5%		1,5-PD[10] 6%	n-BuOH 3%
28	nBC 4%	nHC[11] 1%			
29*	NOAO 4%	NHAO 6%		1,5-PD 6%	peOH[12] 2%
30	NHAO 7%			1,4-BD 5%	BuOH 2%
31	OOAO 6%	S465 0.25%	0.25%	1,4-BD 5%	BuOH 1.75%
32	OOAO 3%	nBC 8%	2.5%		
33*	NOAO 6%	OOAO 2%		1,5-PD 7%	peOH 2%

Notes:
[1]sodium cholate
[2]SURFYNOL 465
[3]n-butanol
[4]n-butyl carbitol
[5]DOWANOL DPM (cellosolve of Dow Chemical Co.)
[6]1,4-butanediol
[7]lithium cholate
[8]PLURONIC L-63
[9]n-butylpropasol
[10]1,5-pentanediol
[11]n-hexyl carbitol
[12]n-pentanol
*These inks have a color bleed index of ≦2.5; the remaining inks have a color bleed index ranging from about 3 to 4.

What is claimed is:

1. A process for reducing color bleed in inks employed in thermal ink-jet printing, comprising printing a first ink on a medium followed by substantially simultaneously printing a second ink adjacent thereto, each said ink having the following composition:

(a) a vehicle; and

(b) about 0.1 to 10 wt% of at least one water-soluble anionic dye dissolved therein,

wherein said vehicle comprises (1) at least one member selected from the group consisting of zwitterionic surfactants and non-ionic amphiphiles, present in an amount that is at least equal to its critical micelle concentration; (2) 0 to about 20 wt% of at least one organic solvent which supports the micelle formation of said at least one member; and (3) the balance water, whereby invasion of one color by another is avoided.

2. The process of claim 1 wherein said zwitterionic surfactants are selected from the group consisting of non-ionic compounds and ionic compounds.

3. The process of claim 2 wherein said non-ionic compounds are selected from the group consisting of water-soluble amphiphile mimetics, polyethers, polyethylene oxides, acetyplenic backboned polyethylene oxides, and amphoteric compounds.

4. The process of claim 3 wherein said mimetics are branched polyethylene amines.

5. The process of claim 3 wherein said polyethers are selected from the group consisting of ethylene glycol n-butyl ether, diethylene glycol n-butyl ether, diethylene glycol n-hexyl ether, triethylene glycol n-butyl ether, and propylene glycol isobutyl ether.

6. The process of claim 3 wherein said amphoteric surfactants are pH-sensitive surfactants selected from the group consisting of N,N-dimethyl-N-dodecyl amine oxide, N,N-dimethyl-N-tetradecyl amine oxide, N,N-dimethyl-N-hexadecyl amine oxide, N,N-dimethyl-N-octadecyl amine oxide, N,N-dimethyl-N-(Z-9-octadecenyl)-N-amine oxide, N-dodecyl-N,N-dimethyl glycine, phosphates, phosphites, phosphonates, lecithins, phosphate esters, phospatidylethanolamines, phosphatidylcholines, phosphatidyl serines, phosphatidylinositos, and B'-O-lysylphosphatidylglycerols.

7. The process of claim 3 wherein said amphoteric surfactants are pH-insensitive surfactants comprising sulfobetaines.

8. The process of claim 2 wherein said ionic surfactants are selected from the group consisting of cetyl trimethylammonium bromide, sodium dodecyl sulfate, sodium sulfonates.

9. The process of claim 1 wherein said organic solvent is selected from the group consisting of glycols, diols, glycol esters, glycol ethers, long chain alcohols, sulfolane esters, ketones, lactones, and glycerols, and derivatives thereof and mixtures thereof.

10. The process of claim 9 wherein said solvent is selected from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, polyethylene glycol, polypropylene glycol, and derivatives thereof; butanediol, pentanediol, hexanediol, and homologous diols; propylene glycol laurate; ethylene glycol monobutyl ether, diethylene glycol mono ethyl ether, diethylene glycol mono butyl ether, diethylene glycol mono hexyl ether, propylene glycol ether, dipropylene glycol ether, and triethylene glycol ether; butyl alcohol, pentyl alcohol, and homologous alcohols; γ-butyrolactone, N-pyrrolidone and N-(2-hydroxyethyl)pyrrolidone, and glycerols and their derivatives.

11. The process of claim 1 wherein said dye is a water-soluble anionic dye selected from the group consisting of C.I. Acid Blue 9, C.I. Acid Red 18, C.I. Acid Red 27, C.I. Acid Red 52, C.I. Acid Yellow 23, C.I. Direct Blue 199, and C.I. Direct Yellow 86.

12. The process of claim 11 wherein said anionic dye is associated with a cation selected from the group consisting of monovalent alkali earth ions, NH_4^+, and substituted ammoniun salts.

13. The process of claim 1 wherein said ink consists essentially of:

about3wt%N,N-dimethyl-N-(Z-9-octadecenyl)-N-amine oxide;

about 0.5wt% of an acetylenic polyethylene oxide surfactant;

about 6wt% pentanediol;

about 3wt% n-butanol;

a dye selected from the group consisting of 1.33wt% Acid Red 27, about 1.33% Direct Yellow 86, and about 1.65wt% Acid Blue 9-Na; and

the balance water.

14. The process of claim 1 wherein said ink consists essentially of:

about 4 wt% N,N-dimethyl-N-octadecyl amine oxide;

about 6 wt% N,N-dimethyl-N-hexadecyl amine oxide;

about 6 wt% pentanedio;

about 2 wt% n-pentanol;

a dye selected from the group consisting of 1.33wt% Acid Red 27, about 1.33wt% Direct Yellow 86, and about 1.65wt% Acid Blue 9-Na; and the balance water.

15. The process of claim 1 wherein said ink consists essentially of:

about 6wt% N,N-dimethyl-N-octadecyl amine oxide;

about2wt% N,N-dimethyl-N-(Z-9-octadecenyl)-N-amine oxide;

about 7wt% pentanediol;

about 2wt% n-pentanol;

a dye selected from the group consisting of 1.33wt% Acid Red 27, about 1.33wt% Direct Yellow 86, and about 1.65wt% Acid Blue 9-Na; and

the balance water.

16. A process for reducing color bleed in inks employed in thermal ink-jet printing, comprising printing a first ink on a medium followed by substantially simultaneously printing a second ink adjacent thereto, each said ink having the following composition:

(a) a vehicle; and

(b) 0.1 to about 10 wt% of at least one water-soluble anionic dye dissolved therein, wherein said vehicle comprises (1) at least one member selected from the group consisting of N,N-dimethyl-N-dodecyl amine oxide N,N-dimethyl-N-hexadecyl amine oxide, N,N-dimethyl-N-octadecyl amine oxide, N,N-dimethyl-N-(z-9-octadecenyl)-N-amine oxide, present in an amount that is at least equal to its critical micelle concentratio; (2) 0 to about 20 wt% of at least one organic solvent selected from the group consisting of pentanediol, pentanol, and butanol; and (3) the balance water, whereby invasion of one color by another is avoided.

17. the process of claim 16 wherein said dye is a water-soluble anionic dye selected from the group consisting of C.I. Acid Blue 9, C.I. Acid Red 18, C.I. Acid Red 27, C.I. Acid Red 52, C.I. Acid Yellow 23, C.I. Direct Blue 199, and C.I. Direct Yellow 86.

18. The process of claim 17 wherein said anionic dye is associated with a cation selected from the group consisting of monovalent alkali earth ions, Nh_4+, and substituted ammonium salts.

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United States Patent [19]
Pawlowski et al.

[11] Patent Number: 5,626,655
[45] Date of Patent: May 6, 1997

[54] **USE OF CO-SURFACTANTS TO ADJUST PROPERTIES OF INK-JET INKS**

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[73] Assignee: **Hewlett-Packard Company**, Palo Alto, Calif.

[21] Appl. No.: **634,057**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 501,262, Jul. 11, 1995, Pat. No. 5,536,306.

[51] **Int. Cl.**[6] **C09D 11/02**
[52] **U.S. Cl.** **106/31.27**; 106/31.43; 106/31.59
[58] **Field of Search** .... 106/22 R, 20 D, 106/22 H

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Primary Examiner—Helene Klemanski

[57] **ABSTRACT**

An ink-jet ink composition is provided which includes at least one primary surfactant and at least one co-surfactant, with the co-surfactant having an HLB at least about 1.5 units higher than that of the primary surfactant. The co-surfactant imparts good wetting and cloud point characteristics to the ink-jet ink composition without sacrificing the bleed control achieved with the use of the low-HLB surfactant. The improvement in wetting and cloud point characteristics achieved in the practice of the invention enables ink-jet printers to effect high print quality in a cost-effective manner. A method for increasing the wettability and cloud point of an ink-jet ink by including at least one co-surfactant having an HLB is also provided.

21 Claims, No Drawings

USE OF CO-SURFACTANTS TO ADJUST PROPERTIES OF INK-JET INKS

CROSS-REFERENCE TO RELATED APPLICATIONS

The present application is a continuation-in-part of the application Ser. No. 08/501,262, filed on Jul. 11, 1995, now U.S. Pat. No. 5,536,306, issued Jul. 16, 1996 in the names of Loren E. Johnson et al and entitled "Thermal Ink-Jet Inks Having Reduced Black to Color and Color to Color Bleed", which is directed to a set of color thermal ink-jet ink compositions evidencing reduced color to color and black to color bleed deriving from a disclosed combination of surfactants and inorganic salts. The present application is also related to application Ser. No. 08/500,759, likewise filed on Jul. 11, 1995, now U.S. Pat. No. 5,534,051, issued Jul. 9, 1996 in the name of Hiang P. Lauw and entitled "Specific Dye Set for Thermal Ink-Jet Printing", which is directed to the use of the tetramethylammonium salt of Direct Blue 199 dye for reduced crusting in the ink set disclosed and claimed therein. Both related applications disclose ink vehicles preferably employing a co-surfactant.

TECHNICAL FIELD

The present invention relates to ink compositions employed in ink-jet printing, especially in thermal ink-jet printing, and, more particularly, to adding a combination of surfactants to ink-jet ink compositions to simultaneously reduce bleed between adjacently-printed colors and to improve wetting and cloud point characteristics.

BACKGROUND ART

Ink-jet printing is a non-impact printing process in which droplets of ink are deposited on print media, such as paper, transparency film, or textiles. Low cost and high quality of output, combined with relatively noise-free operation, have made ink-jet printers a popular alternative to other types of printers used with computers. Essentially, ink-jet printing involves the ejection of fine droplets of ink onto print media in response to electrical signals generated by a microprocessor.

There are two common means currently available for achieving ink droplet ejection in ink-jet printing: thermally and piezoelectrically. In thermal ink-jet printing, the energy for drop ejection is generated by electrically-heated resistor elements, which heat up rapidly in response to electrical signals from a microprocessor to create a vapor bubble, resulting in the expulsion of ink through orifices associated with the resistor elements. In piezoelectric ink-jet printing, the ink droplets are ejected due to the vibrations of piezoelectric crystals, again, in response to electrical signals generated by the microprocessor. The ejection of ink droplets in a particular order forms alphanumeric characters, area fills, and other patterns on the print medium.

Many inks that are described for use in ink-jet printing are associated with non-thermal ink-jet printing, such as piezoelectric ink-jet printing. Inks suitably employed in such non-thermal applications often cannot be used in thermal ink-jet printing due to the effect of heating on the ink composition.

In commercially-available thermal ink-jet color printers, such as a DeskJet® printer available from Hewlett-Packard Company, a color spectrum is achieved by combining cyan, magenta, and yellow inks in various proportions. Ink-jet inks are mostly available as dye-based compositions, although a very limited number of black pigment-based ink-jet inks are also available. Titus, cyan, magenta, and yellow inks typically derive their hues from cyan, magenta, and yellow dyes, respectively. The particular set of dyes so employed constitutes a so-called "dye set". Color printers typically employ a four-pen set containing cyan, magenta, and yellow inks as well as a black ink, which is typically used for printing text.

It follows that color thermal ink-jet inks are commonly available as aqueous-based ink compositions that are formulated by dissolving dye in an ink vehicle. For example, a cyan ink would comprise a cyan dye dissolved in an ink vehicle. The dye molecules employed in ink-jet ink compositions are often in the form of dye salts made of a dye anion and a cation such as sodium. These dyes are designed to form solids in the target paper substrate by absorption into paper media by at least two mechanisms. In one mechanism the dye is wicked into the paper and absorbed onto active sites of the paper fiber. There is another mechanism operating in which the ink vehicle evaporates, or is wicked away from the dye, leaving solid dye on and in paper fibers.

Controlling the behavior of printed ink compositions before absorption of the dye salt in the paper media is crucial in attaining good print quality. For example, many thermal ink-jet inks, when printed in various colors on paper substrates, tend to bleed into one another. The term "bleed", as used herein, is defined to be the invasion of one color into another, as evidenced by a visible ragged border therebetween. To achieve superior print quality, it is necessary to have a border between colors that is clean and free from the invasion of one color into the other.

One solution to the problem of color to color bleed between dye-based ink-jet inks involves increasing the penetration rate of the ink into the paper with the use of surfactants. Surfactants lower the surface tension of the ink to increase the penetration rate of the ink into the print medium, thereby reducing the ink's planar spread across and through the print medium into surrounding inks. To effectively control bleed, the surfactant component should be present in the ink above its critical micelle concentration (cmc), as disclosed in U.S. Pat. No. 5,106,416, entitled "Bleed Alleviation Using Zwitterionic Surfactants and Cationic Dyes", issued to John Moffatt et al and assigned to the same assignee as the present application.

Not all surfactants are effective in controlling color bleed between ink-jet inks: rather, there is a large variance in the effectiveness and behavior of surfactants in ink-jet inks. For example, surfactants differ in their solubility in water and, as a consequence, differ in the form they assume in aqueous ink-jet inks. In an aqueous ink-jet ink, surfactants partition themselves between the following three forms: monolayers, soluble form, and micelles. Surfactants that are :substantially soluble in water form hydrophilic monolayers at liquid-solid interfaces such as that between the ink and the metal nozzle plate. Such surfactants are termed "Gibbs monolayer formers". In contrast, surfactants that are substantially insoluble in water exist as micelles in aqueous solution, since they are essentially dispersed therein: hydrophilic monolayer formation by such surfactants is essentially nonexistent. Rather, such water-insoluble surfactants form water-insoluble monolayers that are hydrophobic in nature and are termed "Langmuir monolayer formers".

One measuring stick of whether a surfactant forms Gibbs monolayers or Langmuir monolayers is its hydrophilic-lipophilic balance (HLB). The HLB value empirically quantifies the balance between the hydrophilic and hydrophobic parts of a surfactant molecule in terms of both size and

strength. HLB values of nonionic surfactants range from 1 to 40, with lower values indicating greater solubility in oil and higher values indicating greater solubility in water.

Regardless of whether a monolayer is hydrophilic or hydrophobic, monolayers of ink on a nozzle plate can develop into bi-layers of ink. Bi-layers form when a second layer of surfactant molecules lay over the monolayer, organizing themselves into a tail-to-tail arrangement thereupon. Both layers of surfactant molecules in a bi-layer formation have their polar heads external to the layer. The likelihood of a monolayer transforming into a bi-layer depends upon the nature of the surfactant and the nature of the material interfacing with the surfactant. More specifically, the formation of bi-layers results in a film surface more compatible with higher energy surfaces.

The degree of surface energy of a material depends on its attractive forces and is expressed in the same units as surface tension. Examples of materials having relatively high surface energies are gold and nickel; orifice plates in ink-jet printers commonly comprise gold, and possibly nickel. Examples of materials having low surface energies are plastics (such as polyethylene) and lipids.

When an aqueous solution containing no surfactant is applied to a surface having low surface energy, the aqueous solution tends to bead up because the low surface energy of the solid cannot pull against the high surface tension of the liquid. By adding a Gibbs-type surfactant to the aqueous solution, the surfactant forms monolayers at the liquid interfaces, both liquid-air and liquid-solid, with the polar head of the surfactant molecule attracted to the aqueous phase and its lipophilic tail pointing out at the interfaces. Such surfactants lower surface tension by disrupting the hydrogen bonding at the aqueous surface and by providing a lipophilic group to mate with the low energy, solid surface.

In ink-jet printing, however, the orifice plate is typically made of a high surface energy material such as gold, and possibly nickel. Therefore, any monolayers formed by surfactants upon the orifice plate would tend to transform into bi-layers given the high surface energy.

Moreover, it has been determined that, especially among nonionic, ionic, and amphoteric surfactants, those having relatively low HLBs offer the best bleed control between ink-jet inks. Specifically, the above-referenced application Ser. No. 08/501,262, now U.S. Pat. No. 5,536,300, discloses the use of primary surfactants that happen to have relatively low HLB values, namely, secondary alcohol ethoxylates such as Tergitol 15-S-5 and Tergitol 15-S-7, which are available from Union Carbide Co. of Houston, Tex. Tergitol 15-S-5 and Tergitol 15-S-7 have HLB values; of about 10.5 and 12.1, respectively. Secondary alcohol ethoxylates contain (a) an aliphatic chain having a prescribed number of carbon atoms in the chain, and (b) a prescribed number of ethoxylated units. Such ethoxylates are commercially available as mixtures of ethoxylates, and so are described in terms of the predominance of a given compound. For example, "Tergitol 15-S-5" represents a secondary alcohol ethoxylate surfactant predominantly having 15 carbons in its aliphatic chain and 5 ethoxylated units. Secondary alcohol ethoxylates suitably employed in Ser. No. 08/501,262 now U.S. Pat. No. 5,536,300 predominantly have about 12 to 18 carbons atoms in the aliphatic chain, while the number of ethoxylated units is predominantly in the range of 4 to 8, and preferably in the range of 5 to 7 units. It is noted that Tergitol 15-S-5, while having a relatively low HLB value, retains some degree of water solubility. Therefore, Tergitol 15-S-5 is not wholly water-insoluble and is not a true "Langmuir monolayer former". For purposes of discussion herein, the Tergitol surfactants are termed "Langmuir-like" monolayer formers, since they impart poor wetting characteristics to aqueous ink solutions, evidenced in the "beading up" of inks containing Tergitol surfactants on metal orifice plate surfaces.

Examples of other surfactants that are successfully employed to control bleed in ink-jet ink compositions include the class of amine oxide surfactants, such as the following: N, N-dimethyl-N-dodecyl amine oxide (NDAO); N,N-dimethyl-N-tetradecyl amine oxide (NTAO); N,N-dimethyl-N-hexadecyl amine oxide (NHAO); N,N-dimethyl-N-octadecyl amine oxide (NOAO); and N,N-dimethyl-N-(9-octadecenyl) amine oxide (OOAO).

It is noted that HLB values for particular surfactants are typically reported as their hydrophilic-lipophilic balances in water, not an aqueous ink system. While the absolute HLB value for a surfactant in water might be a slightly imprecise valuation of its HLB in an aqueous system with 25 wt % co-solvent, the absolute HLB values are still useful in discussing the solubility nature of the surfactant in an aqueous environment. Moreover, it is contemplated that the imprecision in HLB value when employing a co-solvent in an aqueous solution is slight, as evidenced by only a slight increase in cloud point temperature upon adding a co-solvent, as described in greater detail below.

When a surfactant having a relatively low HLB value is dispersed in an aqueous solution, it tends to exist primarily as micelles in solution. At the liquid-solid interface, such surfactants are Langmuir-like monolayer formers and tend to form hydrophobic monolayers, rather than the hydrophilic monolayers formed by relatively high HLB surfactants. When a Langmuir-like monolayer former is employed in an aqueous ink solution along with a high surface energy orifice plate, it tends to form disorganized and hydrophobic monolayers, and sometimes poorly organized bi-layers of surfactant molecules on the liquid-solid interface, with the more polar ends of the surfactant molecules facing toward the solid interface. Consequently, ink containing a surfactant of low HLB, which tends to form monolayers and bi-layers with some Langmuir-type nature, is poorly wetting on a high energy surface such as gold or nickel orifice plates, and the ink will thus form puddles with a high contact angle on these surfaces, rather than wetting with low contact angle and spreading over the gold orifice plate surface.

Wetting characteristics are indicated by contact angle on a given surface, with contact angle being inversely proportional to the degree of wetting imparted to the ink. The formation of puddles evidences a high contact angle on the metal surface, and hence it is concluded that Langmuir-like monolayer formers impart poor wetting characteristics to aqueous ink solutions. In fact, without subscribing to any particular theory, it is speculated that one reason for the relatively low surface tensions of inks containing Tergitol 15-S-5 is the poor wetting of the metal ring used for surface tension measurements, aside from the surfactant's contemplated behavior of disrupting the attractive hydrogen bonding forces at the surface of the liquid.

The poor wetting characteristics of such low HLB surfactants have been found to adversely affect print quality. More particularly, when ink-jet inks made with low-HLB surfactants such as Tergitol 15-S-5 are fired from a thermal ink-jet print cartridge such as one of Hewlett-Packard's DeskJet® printers, the ink tends to form puddles having high contact angles on the metal orifice plates. These puddles of ink may consist of a few small drops of ink or may cover

major portions of the metal orifice plate. Regardless, such high-contact-angle puddles, positioned near any orifice, can cause deflection of ink-jet ink drops jetted through the orifice to a print medium. In severe cases, high-contact-angle puddles of ink on the orifice plate can completely occlude an ink-jet orifice. Thus, while surfactants having low HLB values may be effective in controlling bleed in dye-based ink-jet inks by lowering surface tension, these same surfactants do not provide adequate wetting characteristics to the ink.

An additional problem associated with the use of ethoxylated primary surfactants such as Tergitol surfactants is a reduction in ink temperature cloud point. The cloud point of an ink is that temperature at which the primary surfactant comes out of solution, thereby clouding the visible appearance of the ink, which is an undesirable occurrence. In general, the solubility of surfactants increases with temperature. However, the solubility of these ethoxylated primary surfactants decreases as the temperature is raised, such that their solubility is inversely proportional to the temperature of the ink. It follows that an ink containing a surfactant having a low HLB value which also possesses a polyethyleneoxide group at its solubilizing or polar head has a low temperature cloud point above which the surfactant is insoluble. For example, Tergitol 15-S-5 has such a polyethyleneoxide group and exhibits a temperature cloud point of 29° C., above which temperature the surfactant becomes insoluble.

Tergitol 15-S-5 is the most problematic of the Tergitol surfactants with regard to ink temperature cloud point, but Tergitol 15-S-7 also exhibits this problem to a certain extent. As the number of ethoxylated units increases, the cloud point likewise increases to a more desirable temperature, which is expected given the increased solubility deriving from an increased number of ethoxylated units. It is noted that increasing the concentration of an ethoxylated surfactant in an ink-jet ink increases its solubility in the ink and, consequently, also increases the cloud point temperature.

Accordingly, a need exists for an ink-jet ink composition and method of printing that exhibits improved wetting characteristics and an increased cloud point without sacrificing the bleed control achieved with the use of surfactants having low HLB values.

DISCLOSURE OF INVENTION

In accordance with the invention, an ink-jet ink composition is provided which employs a co-surfactant to achieve good wetting and cloud point characteristics in the ink without sacrificing the bleed control achieved with the use of low-HLB surfactants. More specifically, the ink-jet ink composition comprises at least one dye and a vehicle, with the vehicle including at least one first surfactant and at least one second surfactant, with the hydrophilic-lipophilic balance of the second surfactant being at least about 1.5 units higher than that of the first surfactant. The second surfactant is termed a "co-surfactant" herein.

The first surfactant having the lower HLB value provides bleed control to the ink-jet ink composition but does not impart sufficient wettability to the ink to avoid nozzle plate puddling. Moreover, if a higher HLB co-surfactant is not present to counteract the effects of such low-HLB surfactants, the cloud point temperature of the ink is undesirably low. By employing a co-surfactant in accordance with the invention, one essentially shifts the ink-jet ink toward monolayer formation rather than micelle formation, thereby improving wetting and cloud point characteristics. Specifically, at the ink-orifice plate interface, the addition of a higher HLB co-surfactant provides more polar heads, thereby disrupting the hydrophobic bi-layer film typically formed by low HLB-type surfactants and resulting in better interaction between the bi-layer film and the high energy metal surface. The addition of a higher HLB co-surfactant also improves the ability of an ink-jet pen containing such an ink to recover after being exposed to the atmosphere without a cap.

A method of increasing the wettability and cloud point of an ink-jet ink is also provided which involves formulating an ink-jet ink having the above-described first and second surfactants. Since typical color ink-jet printers employ an ink set having three color inks and a single black ink, it is contemplated that any or all of the four inks may be formulated according to the present invention to achieve high quality priming deriving from (1) reduced print defects due to puddling; (2) clarity of printing due to improved cloud point characteristics; and (3) the retention of bleed alleviation from a low-HLB surfactant. Preferably all four inks in a set of ink-jet inks would be formulated in accordance with the invention for optimum benefit.

The present ink-jet ink compositions and method of increasing the wettability and cloud point of an ink-jet ink may be used with a variety of ink-jet printers such as continuous, piezoelectric drop-on-demand printers and thermal or bubble jet drop-on-demand printers. Printing may be done on a variety of media; examples include paper, textiles, and transparencies. The improvement in wetting and cloud point characteristics achieved in the practice of the invention for ink-jet inks enables ink-jet printers to effect high print quality in a cost-effective manner.

BEST MODES FOR CARRYING OUT THE INVENTION

In the practice of the invention, improved wetting characteristics and increased cloud point temperatures are achieved in ink-jet inks containing surfactants having relatively low HLB values without sacrificing the bleed control attendant to such surfactants. More specifically, a co-surfactant is employed having an HLB exceeding that of the primary surfactant by at least about 1.5 units. The co-surfactant imparts greater wettability to the ink, as evidenced by a lower contact angle between the ink and a metal surface such as an orifice plate. It follows that ink with increased wettability spreads more evenly over the orifice plate. Therefore, not only are such inks less likely to puddle on the orifice plate, but higher wetting inks residing on the orifice plate are more easily drawn back into the print cartridge by back pressure if in contact with the ink meniscus in an orifice.

All concentrations herein are in weight percent, unless otherwise indicated. The purity of all components is that employed in normal commercial practice for ink-jet inks.

The co-surfactants of the present invention are helpful in improving the wetting and cloud point characteristics of inks containing relatively low HLB surfactants. Low HLB surfactants are employed in ink-jet ink compositions to achieve bleed control. More specifically, in above-referenced application Ser. No. 08/501,262, now U.S. Pat. No. 5,536,306, the color inks each include a surfactant component comprising about 1 to 4 wt % of a secondary alcohol ethoxylate surfactant predominantly having 4 to 8 ethoxylated units and an aliphatic chain of about 12 to 18 carbon atoms. Secondary alcohol ethoxylates serve to prevent color to color bleed by increasing the penetration of the inks into the print medium.

Secondary alcohol ethoxylates are nonionic surfactants and are commercially-available, for example, from Union Carbide Co. (Houston, Tex.) as the Tergitol series, such as Tergitol 15-S-5 and Tergitol 15-S-7.

More specifically, secondary alcohol ethoxylates contain (a) an aliphatic chain having a prescribed number of carbon atoms in the chain and (b) a prescribed number of ethoxylated units. These ethoxylates are commercially available as mixtures of ethoxylates, and so are described in terms of the predominance of a given compound. Thus, "Tergitol 15-S-5" represents a secondary alcohol ethoxylate surfactant predominantly having 15 carbons in its aliphatic chain and 5 ethoxylated units. A mixture of secondary alcohol ethoxylates in which the predominant number of ethoxylated units is less than 4 is not very soluble in the ink, while if the predominant number of ethoxylated units is greater than 8, the surfactant loses effectiveness in preventing color bleed. The following table provides HLB values for various mixtures of secondary alcohol ethoxylates:

TABLE 1

HLB Values for Specific Tergitol Surfactants.

Tergitol Surfactant	HLB value
15-S-3	8.0
15-S-5	10.5
15-S-7	12.1
15-S-9	13.3
15-S-12	14.5
15-S-15	15.4
15-S-20	16.3
15-S-30	18.0

Tergitol 15-S-9, with an HLB value of 13.3, represents borderline insolubility in water, while Tergitol 15-S-12 is considered to be soluble in water.

Other classes of surfactants may benefit from the use of co-surfactants, including the class of amine oxide surfactants, such as the following: N, N-dimethyl-N-dodecyl amine oxide (NDAO); N,N-dimethyl-N-tetradecyl amine oxide (NTAO); N,N-dimethyl-N-hexadecyl amine oxide (NHAO); N,,N-dimethyl-N-octadecyl amine oxide (NOAO); and N,N-dimethyl-N-(9-octadecenyl)amine oxide (OOAO).

It is important to note that the class of low HLB-type surfactants targeted in the practice of the invention is not limited to the above-described Tergitol series surfactants and amine oxides. Rather, any surfactant having a relatively low HLB is contemplated to be encompassed by the practice of the invention. Although what is termed a "relatively low HLB" will vary by the type of surfactant, in general, an HLB value is relatively low if it does not exceed 13. Generally, each so-called "class" of surfactants has members of varying HLB values, and according to McCutcheon's Volume 1: Emulsifiers and Detergents (1995 North American Edition), there are approximately sixty (60) classes of surfactants. Accordingly, it is contemplated that there are numerous surfactants having relatively low HLB values that may benefit from association with a higher-HLB co-surfactant in accordance with the invention.

Thus, it is contemplated that the practice of the invention will benefit any inks containing surfactants with relatively low HLB values. Inks containing surfactants with higher HLB values do not experience the same degree of partitioning to micelle formation, but rather are more likely to form monolayers. It is contemplated that the primary, low-HLB-type surfactant ranges in concentration from about 0.5 to 5 wt % of the ink-jet ink composition, although a concentration range of about 1 to 2.5 wt % is preferred for bleed control without degradation of print quality. If the concentration of primary surfactant is too high, the prim quality suffers from loss of edge acuity.

The co-surfactant component may be any surfactant having an HLB value that is at least 1.5 units higher than that of the primary surfactant, thereby countering the primary surfactant's tendency to partition more toward micelle formation and the resulting poor wetting characteristics. Preferably, the HLB of the co-surfactant is at least 2 units higher than that of the primary surfactant, and most preferably 3 units higher. Examples of suitably employed co-surfactants include, but are not limited to, diphenyl disulfonate derivatives, which are anionic surfactants; certain secondary ethoxylated alcohols; and certain amine oxides.

Rather than address the problem of bleed, the presence of this second surfactant serves to correct a sporadic problem that results in mis-directed drops of ink due to puddling of ink on the nozzle plate as a consequence of different surface energies on the nozzle plate. Examples of suitably-employed diphenyl sulfonate derivatives include, but are not limited to: (1) the Calfax family of surfactants, commercially available from Pilot Chemical; (2) Dowfax 8390, a sodium n-hexadecyl diphenyloxide disulfonate commercially available from Dow Chemical having an HLB value of about 14.4; and (3) Poly-Tergent 4C3, a sodium hexadecyl diphenyl ether disulfonate commercially available from Olin Chemical having an HLB value of about 14.4. More specifically, suitable members of the Calfax family of surfactants include Calfax 16L-35, which is a sodium n-hexadecyl diphenyloxide disulfonate having an HLB of about 14.4, and Calfax 10L-45, which is a sodium n-decyl diphenyloxide disulfonate having an HLB of about 17.8.

Examples of secondary ethoxylated alcohols that may be suitably employed as a co-surfactant include, but are not limited to, Tergitols having at least 9 ethoxylated units, although a Tergitol surfactant having 7 ethoxylated units might slightly improve the wetting characteristics of Tergitol 15-S-5. The HLB value of a Tergitol is directly proportional to its number of ethoxylated units. Therefore, while surfactants in Union Carbide's Tergitol family with about 4 to 8 ethoxylated units have low HLB values, Tergitols having more than 9 ethoxylated units have HLB values reflecting at least a borderline solubility in water. The greater the number of ethoxylated units, such as Tergitol 15-S-30 with an HLB of about 18.0 (see Table 1 above), the greater the solubility in water and the more useful the Tergitol is as a co-surfactant.

It is noted that while a Tergitol co-surfactant should essentially have an HLB of more than about 12 (corresponding to at least about 9 ethoxylated units) to properly serve as a co-surfactant in accordance with the invention, this HLB standard is not universal among all classes of surfactants. A surfactant with an HLB of only 12 might be effective in improving wetting characteristics of an ink if the polar group of the surfactant were an amine oxide or a betaine, which are very good zwitterions for interaction with gold surfaces. In comparison, ethoxylated surfactants are not as polar in their wetting, such that the outside surface of the bi-layer does not wet a gold surface as well. Therefore, ethoxylated surfactants typically require higher HLB values to properly serve as co-surfactants in accordance with invention, compared to other types of surfactants such as amine oxides and betaines.

An example of a suitably-employed amine oxide surfactant as a co-surfactant is N-octyldecenyl-N,N-

dimethlyamine oxide, which is commonly known as oleamine oxide and is commercially available from Henkel Corporation under the tradename Standamox 01. Another amine oxide surfactant that may suitable serve as a co-surfactant in accordance with the invention is dimethyl myristyl amine oxide.

It is important to note that the class of high HLB-type surfactants employed as co-surfactants in the practice of the invention is not limited to the above-mentioned diphenyl disulfonate derivatives, Tergitol series surfactants having at least 9 ethoxylated units, and specific amine oxides. Rather, any surfactant having an HLB reflecting some degree of water solubility is contemplated to be capable of serving as a co-surfactant in accordance with the invention. Again, there are approximately sixty (60) accepted classes of surfactants, each of which have surfactants of varying HLB values. Accordingly, it is contemplated that there are numerous surfactants having sufficiently high HLB values that may serve as a co-surfactant in the practice of the invention. Examples of additional classes of surfactants that include suitably-employed co-surfactants are betaines, sorbitan derivatives, sulfonated alkyls, sulfonated alcohols, sulfates of ethoxylated alcohols, and sulfates of ethoxylated alkyls.

The amount of co-surfactant necessary and appropriate for addition to an ink containing a low-HLB surfactant to achieve improved wetting and cloud point characteristics depends upon the amount and type of primary surfactant. One having ordinary skill in the art would be well capable of determining the amount of co-surfactant by simply adding co-surfactant to an ink-jet ink containing a surfactant having a low HLB value until the desired degree of wetting and/or cloud point temperature is attained. As a guideline, the smaller the differential in HLB value between the primary surfactant and the co-surfactant, the higher the concentration of co-surfactant required to achieve the objectives of the invention. It is considered routine experimentation, as opposed to undue experimentation, to determine the appropriate amount of co-surfactant to add to a particular ink system containing a low-HLB surfactant. It is contemplated that the amount of co-surfactant will be within the range of about 0.1 to 0.4 wt % in most applications. As an example, it has been determined that for ink-jet inks containing about 2.25 wt % Tergitol 15-S-5, better wetting is obtained with the addition of 0.1 to 0.25 wt % of a more soluble co-surfactant.

It is noted that an excessive amount of co-surfactant may cause a loss of edge acuity in print quality just as would an excessive amount of primary surfactant. Moreover, co-surfactants do not impart as much bleed control to ink-jet inks in comparison to the primary surfactants. Therefore, an excessive amount of co-surfactant might dominate the surfactant system in an ink-jet ink and have an adverse effect on overall print quality. It is contemplated that the definition of what is "excessive" will vary with each co-surfactant. However, as an example, it has been determined that Calfax 10L-45 may be employed up to about 0.5 wt % of an ink-jet ink composition as a co-surfactant. Above 0.5 wt % of Calfax 10L-4.5, a loss in print quality due to reduced edge acuity and bleed control is readily apparent.

It is noted that surface tension alone does not indicate the wetting tendencies of an ink and therefore cannot be used to assess the need for a co-surfactant. In fact, the addition of a co-surfactant in accordance with the invention will likely increase the surface tension of the ink. For example, an ink having the following composition has a surface tension of 28.5 dyne/cm: (a) 3 wt % dye; (b) 8 wt % 1,5-pentanediol; (c) 7.5 wt % ethylhydroxypropanediol; (d) 7.5 wt % 2-pyrrolidone; (e) 6 wt % $Mg(NO_3)_2 \bullet 6H_2O$; (f) 2.0 wt % Tergitol 15-S-5; (g) 0.2 wt % each of biocide and buffer; and (h) the balance water. Upon adding about 0.25 wt % of either Calfax 10L-45 or about 0.25 wt % Tergitol 15-S-30, the surface tension increases to 29.4 dyne/cm. However, the wetting characteristics of the ink improve as evidenced by visual inspection of the contact angle of the ink with a metal surface. The increase in surface tension may be due to the nature of monolayers at the liquid-air interface, where surface tension is measured. Alternatively, the increase in surface tension may be due to the film interacting poorly with the platinum ring used to measure surface tension.

While it is contemplated that the present co-surfactant may benefit any ink-jet ink having a relatively low HLB, such as less than about 13, color ink-jet inks comprising the following components are specifically contemplated: (a) about 0.1 to 4 wt % of at least one dye; (b) about 3 to 20 wt % of at least one diol; (c) 0 to about 5 wt % of at least one glycol ether; (d) about 3 to 9 wt % of 2-pyrrolidone; (e) up to about 4 wt % of at least one component selected from the group consisting of biocides and buffers; (f) about 1 to 4 wt % of a first surfactant consisting essentially of at least one secondary alcohol ethoxylate surfactant predominantly having 4 to 8 ethoxylated units and an aliphatic chain having about 12 to 18 carbon atoms; (g) about 3 to 6 wt % of at least one inorganic salt component (for black to color bleed); and (h) water. Thus, in the practice of the invention, it is contemplated that between about 0.1 and 0.4 wt % of a co-surfactant is added to the preceding ink composition to improve the wetting and cloud point characteristics thereof.

It is contemplated that any dye that is compatible with the remaining components of the ink-jet ink composition may be employed in the practice of the invention. Examples of suitable dyes include, but are not limited to, Acid Blue 9, Direct Blue 199, Reactive Red 180, Acid Red 52, and Acid Yellow 23.

Diols preferably employed in the present ink-jet ink compositions include any of, or a mixture of two or more of, such compounds as ethanediols (e.g., 1,2-ethanediol); propanediols (e.g., 1,2-propanediol, 1,3-propanediol, 2-ethyl-2-hydroxy-methyl-1,3-propanediol, ethylhydroxypropanediol (EHPD), etc.); butanediols (e.g., 1,3-butanediol, 1,4-butanediol, etc.); pentanediols (e.g., 1,5-pentanediol); and hexanediols (e.g., 1,6-hexanediol, 2,5-hexanediol, etc.). Preferably, 1,5-pentanediol and EHPD are employed in the practice of the invention.

The glycol ether component preferably employed in the present ink vehicle includes any of the glycol ethers and thioglycol ethers commonly employed in the inks used in ink-jet printing, or a mixture thereof. Examples of such compounds include polyalkylene glycols such as polyethylene glycols (e.g., diethylene glycol, triethylene glycol, tetraethylene glycol, etc.); polypropylene glycols (e.g., dipropylene glycol, tripropylene glycol, tetrapropylene glycol, etc.); polymeric glycols (e.g., PEG 200, PEG 300, PEG 400, PPG 400, etc.); and thiodiglycol. More preferably, diethylene glycol is employed.

Preferably, the concentration of pentanediol and glycol component in each color ink is given by the formula

$$2\times[DEG]+[pentanediol]=\text{about 6 to 10 wt \%},$$

where the square brackets denote the concentration in weight percent. For the more preferred cyan and magenta ink compositions, DEG is absent and 1,5-pentanediol is present in the range of about 7 to 9 wt %, and most preferably about 7.5 to 8.5 wt %. For the more preferred yellow ink composition, the amount of DEG ranges from

about 3 to 5 wt % and most preferably about 3.5 to 4.5 wt %, and 1.5-pentanediol is absent.

EHPD is considered separately and is present in each ink in an amount in the range of about 6 to 9 wt %. For the cyan and magenta inks, EHPD is preferably present within the range of about 7 to 8 wt %, while for the yellow ink, EHPD is preferably present within the range of about 7.5 to 8.5 wt %.

Consistent with the requirements for this invention, various types of other additives may be employed in the ink to optimize the properties of the ink composition for specific applications. For example, as is well known to those skilled in the art, one or more biocides, fungicides, and/or slimicides (microbial agents) may be used in the ink composition as is commonly practiced in the art. Any of the biocides commonly employed in ink-jet inks may be employed in the practice of the invention, such as NUOSEPT 95, available from Hüls America (Piscataway, N.J.); PROXEL GXL, available from ICI America (Wilmington, Del.); and glutaraldehyde, available from Union Carbide Company (Bound Brook, N.J.) under the trade designation UCARCIDE 250. PROXEL GXL is the preferred biocide. Additionally, sequestering agents such as EDTA may be included to eliminate deleterious effects of heavy metal impurities, and buffer solutions may be used to control the pH of the ink. Other known additives such as viscosity modifiers and other acrylic or non-acrylic polymers may be added to improve various properties of the ink compositions as desired.

Buffers employed to modulate pH of the present preferred ink composition should be organic-based biological buffers, since inorganic buffers, if employed, would likely precipitate in the presence of the relatively large amount of inorganic salts in the ink composition. Further, the buffer employed should provide a pH ranging from about 6 to 9 in the practice of the invention. Examples of preferably-employed buffers include 2-amino-2-(hydroxymethyl)-1,3-propanediol (Trisma Base), which is available from, for example, Aldrich Chemical (Milwaukee, Wis.), and 2-[N-morpholino]-ethanesulfonic acid (MES), sodium salt.

The amount of the secondary alcohol ethoxylate preferably employed in the final ink-jet ink composition is given by the sum of the two Tergitol components, 15-S-5 and 15-S-7, according to the formula

$$[15\text{-S-5}]+[15\text{-S-7}]=\text{about 1 to 4 wt \%},$$

where the square brackets denote the concentration in weight percent. Preferably, Tergitol 15-S-5 alone is present in the cyan and magenta inks in the range of about 1.5 to 3 wt % and most preferably about 1.5 to 2.5 wt %. In the yellow ink, a mixture of the two Tergitols is preferably employed, with 15-S-5 ranging from about 0.5 to 2 wt % and 15-S-7 ranging from about 1 to 2 wt %; in the most preferred case for the yellow ink, 15-S-5 ranges from about 0.8 to 1.2 wt % and 15-S-7 ranges from about 1.3 to 1.7 wt %.

The metal salt component of the preferred ink vehicle serves to prevent bleed between black ink and the color inks, and comprises one or more inorganic salts. The salts must, of course, be soluble in the ink in the concentration employed. Suitably-employed cations for the salt include alkaline earth metals of group 2A of the periodic table (e.g., magnesium and calcium); the transition metals of group 3B of the periodic table (e.g., lanthanum); cations from group 3A of the periodic table (e.g., aluminum); and lanthanides (e.g., neodymium). Preferably, calcium and magnesium are employed as cations in the practice of the invention. Suitably-employed anions associated with calcium include nitrate, chloride, acetate, benzoate, formate, and thiocyanate, while suitable anions associated with magnesium include nitrate, chloride, acetate, benzoate, bromide, citrate, formate, iodide, sulfate, fluoride, tartrate, and thiocyanate. Salts preferably employed in the practice of the invention are the nitrate, chloride, and acetate salts of calcium and magnesium. More specifically, the cyan and magenta inks of the present invention preferably employ magnesium nitrate while the yellow ink preferably employs calcium nitrate.

Finally, another optional component that may be employed in the present ink vehicles is ammonium nitrate, which is used in conjunction with calcium-containing inorganic salts. Ammonium nitrate serves to prevent the precipitation of such calcium-containing inorganic salts in the ink upon exposure to the carbon dioxide in the air.

Anti-kogation of the inks is achieved by well-known substitution of cations on certain dyes with other cations. For example, sodium cations associated with Direct Blue 199 (used in the cyan ink) are substantially totally replaced with tetramethyl ammonium (TMA) cations, while sodium cations associated with Acid Red 52 (used in the magenta ink) are substantially totally replaced with lithium cations, and sodium cations associated with Acid Yellow 23 (used in the yellow ink) are substantially totally replaced with TMA cations.

Therefore, cyan ink is preferably formulated by combining purified Acid Blue 9 and Direct Blue 199 anionic dyes with the above-described preferred ink vehicle, the latter dye being particularly known for providing high light fastness. Given the relatively high metal salt concentration in the cyan ink, Direct Blue 199 associated with sodium or ammonium would likely precipitate out of the vehicle. Thus, Direct Blue 199 is treated to substantially replace all or most of the as-supplied sodium or ammonium cation with TMA cation. The Acid Blue 9 anionic dye may remain associated with sodium in the practice of the invention. The substitution of TMA in Direct Blue 199 reduces crusting about the orifice attributable to cyan ink and enables the cyan ink to remain in solution in the presence of a relatively high concentration of inorganic salts. Since the Acid Blue 9 anionic dye may remain associated with sodium in the practice of the invention, the amount of Acid Blue 9 must be limited such that the presence of its associated sodium cation does not undo the benefits achieved by replacing the sodium or ammonium cation of Direct Blue 199 with TMA. Preferably, Direct Blue 199 and Acid Blue 9 are employed at concentrations ranging from about 2 to 3 wt % and 1 to 2 wt %, respectively. More preferably, the ratio of the concentration of Direct Blue 199 dye to the concentration of Acid Blue 9 dye in the present cyan ink is about 2:1 by weight.

A variety of methods may be used to replace the sodium or ammonium ion associated with Direct Blue 199 with TMA. Examples of such ion-exchange processes are disclosed in U.S. Pat. Nos. 4,685,968 and 4,786,327, both assigned to the same assignee as the present invention. The method of forming the TMA form of the DB 199 dye forms no part of this invention.

All told, the cyan ink is preferably prepared according to the following formulation and buffered to a pH of about 8:

(a) about 0.1 to 4 wt % of a mixture of Direct Blue 199-TMA and Acid Blue 9-Na, with Direct Blue 199-TMA more preferably present at about 2 to 3 wt % and Acid Blue 9-Na more preferably present at about 1 to 2 wt %, most preferably with the ratio by weight of Direct Blue 199 to Acid Blue 9 being about 2:1;

(b) a mixture of DEG and 1,5-pentanediol given by the formula

2×[DEG]+[pentanediol]=about 6 to 10 wt %

and about 6 to 9 wt % ethylhydroxypropanediol (EHPD), with 1,5-pentanediol being more preferably present at about 7 to 9 wt % (and DEG absent) and most preferably about 7.5 to 8.5 wt %, and with EHPD being preferably present at about 7 to 8 wt % of the ink composition;

(c) about 3 to 9 wt % of 2-pyrrolidone, with about 6 to 9 wt % being more preferable and about 7 to 8 wt % being most preferable;

(d) about 3 to 6 wt % of a mixture of magnesium nitrate and/or calcium nitrate, with 4 to 5 wt % magnesium nitrate alone being more preferable;

(e) about 1 to 4 wt % of a mixture, of Tergitol 15-S-5 and/or Tergitol 15-S-7, with Tergitol 15-S-5 being more preferably employed alone ranging from about 1.5 to 3 wt % or, most preferably, 1.5 to 2.5 wt %;

(f) up to about 0.4 wt % of Dowfax 8390 surfactant, with about 0.3 to 0.4 wt % being more preferable;

(g) about 0.1 to 1 wt % of a buffer, preferably Trisma Base or MES, more preferable Trisma Base;

(h) up to about 1 wt % of a biocide, preferably PROXEL GXL; and

(i) the balance water.

The magenta ink employed in the practice of the invention is preferably formulated by combining purified Reactive Red 180 in its hydrolyzed form and purified Acid Red 52 anionic dye with an ink vehicle comprised of the above-described components and concentration ranges. The Acid Red 52 anionic dye is preferably treated to replace the as-supplied sodium cation with lithium. Preferably, the ratio of the concentration of Reactive Red 180 to the concentration of Acid Red 52 in the present magenta ink is about 1:1 by weight. Any of a variety of methods may be used to replace the sodium ion associated with Acid Red 52 with lithium, such as an ion-exchange process. The method of forming the lithium form of the dye forms no part of this invention.

Preferably, the magenta ink is prepared according to the following formulation and is buffered to a pH of about 7:

(a) about 0.1 to 4 wt % of a mixture of Reactive Red 180 and Acid Red 52-Li, with the ratio by weight of Reactive Red 180 to Acid Red 52 being more preferably about 1:1;

(b) a mixture of DEG and 1,5-pentanediol given by the formula

2×[DEG]+[pentanediol]=about 6 to 10 wt %

and about 6 to 9 wt % ethylhydroxypropanediol (EHPD), with 1,5-pentanediol being more preferably present at about 7 to 9 wt % (and DEG absent) and most preferably about 7.5 to 8.5 wt %, and with EHPD being preferably present at about 7 to 8 wt % of the ink composition;

(c) about 3 to 9 wt % of 2-pyrrolidone, with about 6 to 9 wt % being more preferable and about 7 to 8 wt % being most preferable;

(d) about 3 to 6 wt % of a mixture: of magnesium nitrate and/or calcium nitrate, with 4 to 5 wt % magnesium nitrate alone being more preferable;

(e) about 1 to 4 wt % of a mixture: of Tergitol 15-S-5 and/or Tergitol 15-S-7, with Tergitol 15S-5 being more preferably employed alone ranging from about 1.5 to 3 wt % or, most preferably, 1.5 to 2.5 wt %;

(f) up to about 0.4 wt % of Dowfax 8390 surfactant, with about 0.3 to 0.4 wt % being more preferable;

(g) about 0.1 to 1 wt % of a buffer, preferably Trisma base or MES, more preferably MES;

(h) up to about 1 wt % of a biocide, preferably PROXEL GXL; and

(i) the balance water.

The yellow ink employed in the practice of the invention is formulated by combining purified Acid Yellow 23 anionic dye with an ink vehicle comprising the above-described components and concentration ranges. The Acid Yellow 23 anionic dye is preferably treated to replace the as-supplied sodium cation with tetramethylammonium, which may be accomplished by a process such as ion-exchange. The method of forming the TMA form of the dye forms no part of this invention.

Preferably, the yellow ink is prepared according to the following formulation and buffered to a pH of about 6.5:

(a) about 0.1 to 4 wt % of Acid Yellow 23-TMA;

(b) a mixture of DEG and 1,5-pentanediol given by the formula

2×[DEG]+[pentanediol]=about 6 to 10 wt %

and about 6 to 9 wt % ethylhydroxypropanediol, with the DEG being more preferably present in the mixture at about 3 to 5 wt % (and 1,5 pentanediol absent) and most preferably about 3.5 to 4.5 wt %, and the ethylhydroxypropanediol being more preferably present at about 7.5 to 8.5 wt %;

(c) about 3 to 9 wt % of 2-pyrrolidone, with about 3 to 5 wt % being more preferable and about 3.5 to 4.5 wt % being most preferable;

(d) about 3 to 6 wt % of a mixture of magnesium nitrate and/or calcium nitrate, with 4 to 5 wt % calcium nitrate alone being more preferable;

(e) about 1 to 4 wt % of a mixture, of Tergitol 15-S-5 and/or Tergitol 15-S-7, with a mixture of about 0.5 to 2 wt % Tergitol 15-S-5 and about 1 to 2 wt % Tergitol 15-S-7 being more preferable or, most preferably, a mixture of about 0.8 to 1.2 wt % Tergitol 15-S-5 and about 1.3 to 1.7 wt % Tergitol 15-S-7;

(f) up to about 0.4 wt % of Dowfax 8390 surfactant, with about 0.3 to 0.4 wt % being more preferable;

(g) about 0.1 to 1 wt % of a buffer, preferably Trisma base or MES;

(h) up to about 1 wt % of a biocide, preferably PROXEL GXL; and

(i) the balance water.

Finally, the black ink employed along with the above-described color ink-jet inks may be any dye-based or a pigment-based ink that is suitably employed in thermal ink-jet printing. Suitable black dye-based inks are disclosed and claimed, for example, in U.S. Pat. No. 4,963,189, entitled "Waterfast Ink Formulations with a Novel Series of Anionic Dyes Containing Two or More Carboxyl Groups" and assigned to the present assignee. Suitable black pigment-based inks are disclosed and claimed, for example, in U.S. Pat. No. 5,085,698, entitled "Aqueous Pigmented Inks for Ink Jet Printers", in U.S. Pat. No. 5,221,334, entitled "Aqueous Pigmented Inks for Ink Jet Printers", and in U.S. Pat. No. 5,302,197, entitled "Ink Jet Inks", all assigned to E. I. Du Pont de Nemours and Company.

Ink-jet ink compositions containing a first surfactant with a relatively low HLB that are formulated in accordance with the invention to also comprise a second surfactant with an HLB that is at least about 1.5 units higher will exhibit improved wetting and cloud point characteristics while retaining their bleed-alleviation characteristics.

In addition to improving wetting and cloud point temperature, the addition of a higher HLB co-surfactant improves the ability of an ink-jet pen containing such an ink to recover after being exposed to the atmosphere without a cap. Generally, surfactants having higher HLB values are more soluble and decrease the tendency for hard plugs to form in the ink-jet printer nozzles. Specifically, hard plugs form from the solid ingredients in an ink composition in the manner of residue remaining when the volatiles such as water evaporate from ink. Surfactants having more polar heads, i.e. higher HLB values, have a greater tendency to hold water of hydration.

The examples below demonstrate the improved wetting and cloud point characteristics achieved in the practice of the invention.

EXAMPLES

To demonstrate the effectiveness of a high-HLB co-surfactant in imparting wettability to an ink-jet ink containing a low-HLB surfactant, the following cyan ink-jet ink was formulated:

(a) about 1.2 wt % Acid Blue 9-Na and about 2 wt % Direct Blue 199-TMA;

(b) about 8 wt % 1,5-pentanediol;

(c) about 7.5 wt % 2-pyrrolidone;

(d) about 7.5 wt % ethylhydroxypropanediol;

(e) about 6 wt % of $Mg(NO_3)_2 \bullet H_2O$;

(f) about 2.25 wt % Tergitol 15-S-5;

(g) about 0.2 wt % each of Trisma Base and Proxel GXL; and

(h) the balance water.

The above-described ink-jet ink composition had a surface tension of about 29.4 dynes/cm and a contact angle of roughly about 100° on gold, the angle having been visually estimated. Given the low wettability of this ink, it exhibited unacceptable print defects deriving from puddle formation on the orifice plate while printing. In accordance with the invention, about 0.25 wt % of Tergitol 15-S-5 was replaced with about 0.25 wt % Calfax 16L-35, with the resulting ink-jet ink composition having a surface tension of about 30.5 dyne/cm and a reduced contact angle of roughly about 2° or less on gold, as visually estimated. This increase in wettability greatly reduced puddling on the orifice plate such that a substantial reduction in print defects was achieved, along with an overall improvement in print quality.

To demonstrate the effectiveness of a high-HLB co-surfactant in increasing the cloud point temperature of an ink-jet ink containing a low-HLB co-surfactant, the above-described ink, which had a cloud point temperature of about 29° C., was formulated with various types and concentrations of co-surfactants as provided below in Table 2:

TABLE 2

Effect on Cloud Point of Ink-Jet Ink by Co-Surfactants.

Co-Surfactant	Concentration, wt %	Cloud Point, °C.
None	0.0	29
Calfax 10L-45	0.12	40
Calfax 10L-45	0.25	50
Calfax 10L-45	0.34	61–61.5
Calfax 10L-45	0.5	74–75
Calfax 10L-45	0.75	91–92
Tergitol 15-S-30	0.25	52
N-octyldecenyl-N,N-dimethylamine oxide	0.25	38

Therefore, it is demonstrated that by adding the indicated concentrations of co-surfactant, an increase in cloud point

temperature is achieved. Given that the base cloud point was only 29° C., the ink without co-surfactant would regularly suffer from cloudiness in thermal ink-jet priming.

Thus, it has been demonstrated that the addition of a proper amount of co-surfactant can impart improved wetting and cloud point characteristics to an ink-jet ink containing a surfactant having a relatively low HLB, thereby improving overall print quality by minimizing both precipitation of the low-HLB surfactant as well as print defects due to ink puddling on the orifice plate.

INDUSTRIAL APPLICABILITY

The present ink-jet ink compositions and method of increasing wettability and cloud point of an ink-jet ink as disclosed herein are expected to find commercial use in ink-jet printing.

Thus, there has been disclosed an ink-jet ink composition which exhibits improved wetting and cloud point characteristics by employing a co-surfactant having a relatively higher HLB value that is complementary to a primary surfactant having a low HLB value. A method of increasing wettability and cloud point in an ink-jet ink is also disclosed which employs such an ink-jet ink composition to achieve improved print quality. It will be readily apparent to those skilled in the art that various changes and modifications of an obvious nature may be made without departing from the spirit of the invention, and all such changes and modifications are considered to fall within the scope of the invention as defined by the appended claims.

What is claimed is:

1. An ink-jet ink composition comprising at least one substantially water-soluble dye and a vehicle, said vehicle including at least one first surfactant and at least one second surfactant, said at least one second surfactant having a hydrophilic-lipophilic balance that is at least about 1.5 units higher than that of said at least one first surfactant.

2. The ink-jet ink composition of claim **1** wherein said at least one first surfactant has a hydrophilic-lipophilic balance of less than about 13 and wherein said at least one second surfactant has a hydrophilic-lipophilic balance of at least about 12.

3. The ink-jet ink composition of claim **2** wherein said at least one first surfactant is a secondary alcohol ethoxylate surfactant predominantly having 4 to 8 ethoxylated units.

4. The ink-jet ink composition of claim **3** wherein said secondary alcohol ethoxylate surfactant has an aliphatic chain of about 12 to 18 carbon atoms.

5. The ink-jet ink of claim **4** wherein said secondary alcohol ethoxylate surfactant is selected from the group consisting of secondary alcohol ethoxylate surfactant predominantly having 5 ethoxylated units and an aliphatic chain of about 15 carbon atoms, a secondary alcohol ethoxylated surfactant predominantly having 7 ethoxylated units and an aliphatic chain of about 15 carbon atoms, and mixtures thereof.

6. The ink-jet ink composition of claim **1** wherein said at least one first surfactant is present in said ink-jet ink composition at a concentration ranging from about 0.5 to 5 wt % of said ink-jet ink composition.

7. The ink-jet ink composition of claim **1** wherein said at least one second surfactant is selected from the group consisting of diphenyl sulfonate derivatives, secondary ethoxylated alcohols, amine oxides, betaines, sorbitan derivatives, sulfonated alkyls, sulfonated alcohols, sulfates of ethoxylated alcohols, and sulfates of ethoxylated alkyls.

8. The ink-jet ink composition of claim **7** wherein said diphenyl sulfonate derivatives are selected from the group

consisting of an n-hexadecyl diphenyloxide disulfonate, an hexadecyl diphenyl ether disulfonate, and an n-decyl diphenyloxide disulfonate; wherein said secondary ethoxylated alcohols are selected from the group consisting of secondary ethoxylated alcohol surfactants predominantly having at least about 9 ethoxylated units; and wherein said amine oxides are selected from the group consisting of N-octyldecenyl-N,N-dimethlyamine oxide and dimethyl myristyl amine oxide.

9. The ink-jet ink composition of claim **1** wherein said at least one second surfactant is present in said ink-jet ink composition at a concentration ranging from about 0.1 to 0.4 wt % of said ink-jet ink composition.

10. The ink-jet ink composition of claim **1** wherein said at least one second surfactant has a hydrophilic-lipophilic balance that is at least about 3 units higher than that of said at least one first surfactant.

11. A method of increasing the wettability and cloud point of an ink-jet ink for ink-jet printing, said ink-jet ink comprising at least one substantially water-soluble dye and a vehicle, said vehicle including at least one first surfactant, wherein said method comprises formulating said ink-jet ink to further include at least one second surfactant having a hydrophilic-lipophilic balance that is at least about 1.5 units higher than that of said at least one first surfactant.

12. The method of claim **11** wherein said at least one first surfactant has a hydrophilic-lipophilic balance of less than about 13 and wherein said at least one second surfactant has a hydrophilic-lipophilic balance of at least about 12.

13. The method of claim **12** wherein said at least one first surfactant is a secondary alcohol ethoxylate surfactant predominantly having 4 to 8 ethoxylated units.

14. The method of claim **13** wherein said secondary alcohol ethoxylate surfactant has an aliphatic chain of about 12 to 18 carbon atoms.

15. The method of claim **14** wherein said secondary alcohol ethoxylate surfactant is selected from the group consisting of secondary alcohol ethoxylate surfactant predominantly having 5 ethoxylated units and an aliphatic chain of about 15 carbon atoms, a secondary alcohol ethoxylated surfactant predominantly having 7 ethoxylated units and an aliphatic chain of about 15 carbon atoms, and mixtures thereof.

16. The method of claim **11** wherein said at least one first surfactant is present in said ink-jet ink composition at a concentration ranging from about 0.5 to 5 wt % of said ink-jet ink composition.

17. The method of claim **11** wherein said at least one second surfactant is selected from the group consisting of diphenyl sulfonate derivatives, secondary ethoxylated alcohols, amine oxides, betaines, sorbitan derivatives, sulfonated alkyls, sulfonated alcohols, sulfates of ethoxylated alcohols, and sulfates of ethoxylated alkyls.

18. The method of claim **17** wherein said diphenyl sulfonate derivatives are selected from the group consisting of an n-hexadecyl diphenyloxide disulfonate, an hexadecyl diphenyl ether disulfonate, and an n-decyl diphenyloxide disulfonate; wherein said secondary ethoxylated alcohols are selected from the group consisting of secondary ethoxylated alcohol surfactants predominantly having at least about 9 ethoxylated units; and wherein said amine oxides are selected from the group consisting of N-octyldecenyl-N,N-dimethlyamine oxide and dimethyl myristyl amine oxide.

19. The method of claim **11** wherein said at least one second surfactant is present in said ink-jet ink at a concentration ranging from about 0.1 to 0.4 wt %.

20. The method of claim **11** wherein said at least one second surfactant has a hydrophilic-lipophilic balance that is at least about 3 units higher than that of said at least one first surfactant.

21. A color ink-jet printer including a set of cyan, yellow, magenta, and black inks, each ink having a composition comprising at least one dye and a vehicle, said vehicle including at least one first surfactant and at least one second surfactant, said at least one second surfactant having a hydrophilic-lipophilic balance that is at least about 1.5 units higher than that of said at least one first surfactant.

* * * * *

JS 44 (Rev. 12/07) (cand rev 1-16-08)

CIVIL COVER SHEET

The JS 44 civil cover sheet and the information contained herein neither replace nor supplement the filing and service of pleadings or other papers as required by law, except as provided by local rules of court. This form, approved by the Judicial Conference of the United States in September 1974, is required for the use of the Clerk of Court for the purpose of initiating the civil docket sheet. (SEE INSTRUCTIONS ON PAGE TWO OF THE FORM.)

ADR

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C08 02596 PVT

I. (a) PLAINTIFFS

HEWLETT-PACKARD COMPANY, a Delaware corporation

DEFENDANTS

LEXJET CORPORATION, a Florida corporation, and LEXJET SOUTHERN CALIFORNIA, LLC, a California limited liability company

(b) County of Residence of First Listed Plaintiff
(EXCEPT IN U.S. PLAINTIFF CASES)

County of Residence of First Listed Defendant Sarasota County, Florida
(IN U.S. PLAINTIFF CASES ONLY)
NOTE: IN LAND CONDEMNATION CASES, USE THE LOCATION OF THE LAND INVOLVED.

(c) Attorney's (Firm Name, Address, and Telephone Number)

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Palo Alto, CA 94306
Telephone: 650.843.4000

Attorneys (If Known)

II. BASIS OF JURISDICTION (Place an "X" in One Box Only)

- [ ] 1 U.S. Government Plaintiff
- [X] 3 Federal Question (U.S. Government Not a Party)
- [ ] 2 U.S. Government Defendant
- [ ] 4 Diversity (Indicate Citizenship of Parties in Item III)

III. CITIZENSHIP OF PRINCIPAL PARTIES (Place an "X" in One Box for Plaintiff and One Box for Defendant) (For Diversity Cases Only)

	PTF	DEF		PTF	DEF
Citizen of This State	[ ] 1	[ ] 1	Incorporated *or* Principal Place of Business In This State	[ ] 4	[ ] 4
Citizen of Another State	[ ] 2	[ ] 2	Incorporated *and* Principal Place of Business In Another State	[ ] 5	[ ] 5
Citizen or Subject of a Foreign Country	[ ] 3	[ ] 3	Foreign Nation	[ ] 6	[ ] 6

IV. NATURE OF SUIT (Place an "X" in One Box Only)

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- [ ] 130 Miller Act
- [ ] 140 Negotiable Instrument
- [ ] 150 Recovery of Overpayment & Enforcement of Judgment
- [ ] 151 Medicare Act
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- [ ] 153 Recovery of Overpayment of Veteran's Benefits
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- [ ] 190 Other Contract
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- [ ] 210 Land Condemnation
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- [ ] 230 Rent Lease & Ejectment
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- [ ] 315 Airplane Product Liability
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- [ ] 330 Federal Employers' Liability
- [ ] 340 Marine
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- [ ] 350 Motor Vehicle
- [ ] 355 Motor Vehicle Product Liability
- [ ] 360 Other Personal Injury

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- [ ] 365 Personal Injury — Product Liability
- [ ] 368 Asbestos Personal Injury Product Liability

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- [ ] 535 Death Penalty
- [ ] 540 Mandamus & Other
- [ ] 550 Civil Rights
- [ ] 555 Prison Condition

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- [ ] 620 Other Food & Drug
- [ ] 625 Drug Related Seizure of Property 21 USC 881
- [ ] 630 Liquor Laws
- [ ] 640 R.R. & Truck
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- [ ] 690 Other

LABOR
- [ ] 710 Fair Labor Standards Act
- [ ] 720 Labor/Mgmt. Relations
- [ ] 730 Labor/Mgmt.Reporting & Disclosure Act
- [ ] 740 Railway Labor Act
- [ ] 790 Other Labor Litigation
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- [ ] 463 Habeas Corpus – Alien Detainee
- [ ] 465 Other Immigration Actions

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- [ ] 423 Withdrawal 28 USC 157

PROPERTY RIGHTS
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- [X] 830 Patent
- [ ] 840 Trademark

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- [ ] 864 SSID Title XVI
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- [ ] 895 Freedom of Information Act
- [ ] 900 Appeal of Fee Determination Under Equal Access to Justice
- [ ] 950 Constitutionality of State Statutes

V. ORIGIN (Place an "X" in One Box Only)

- [X] 1 Original Proceeding
- [ ] 2 Removed from State Court
- [ ] 3 Remanded from Appellate Court
- [ ] 4 Reinstated or Reopened
- [ ] 5 Transferred from another district (specify)
- [ ] 6 Multidistrict Litigation
- [ ] 7 Appeal to District Judge from Magistrate Judgment

VI. CAUSE OF ACTION

Cite the U.S. Civil Statute under which you are filing (**Do not cite jurisdictional statutes unless diversity**):
35 U.S.C. § 1, et seq.

Brief description of cause:
Patent infringement.

VII. REQUESTED IN COMPLAINT:

- [ ] CHECK IF THIS IS A CLASS ACTION UNDER F.R.C.P. 23

DEMAND $ 0.00

CHECK YES only if demanded in complaint:
JURY DEMAND: [X] Yes [ ] No

VIII. RELATED CASE(S) IF ANY

PLEASE REFER TO CIVIL L.R. 3-12 CONCERNING REQUIREMENT TO FILE "NOTICE OF RELATED CASE". JUDGE JAMES WARE, CASE NO. 94-CV-20647

IX. DIVISIONAL ASSIGNMENT (CIVIL L.R. 3-2) (PLACE AND "X" IN ONE BOX ONLY)

- [ ] SAN FRANCISCO/OAKLAND
- [ ] SAN JOSE

DATE May 22, 2008

SIGNATURE OF ATTORNEY OF RECORD